PROGRESS IN THE CHEMISTRY OF FATS AND OTHER LIPIDS

Volume 5

ADVANCES IN TECHNOLOGY

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PREFACE

WHEN this series on *Progress in the Chemistry of Fats and Other Lipids* was started, it was planned that it should contain brief monographs dealing only with the purely chemical and biochemical aspects of lipids. Monographs concerning technology were to be brought together in an entirely separate series entitled *Progress in the Technology of Fats*.

Relatively frequent volumes on chemical and biochemical advances appear to be well justified, but it is now evident that such is not the case with technological advances, in spite of rapid progress in technology. Further, probably a majority of those who are associated with the lipids field have interests that cut across both scientific and technological areas. For these reasons, the editors have decided that, whenever it appears desirable to summarize recent advances in technology, monographs will be brought together in a special volume on technology to be included in the series on *Progress in the Chemistry of Fats and Other Lipids*.

The chapters that are included in this volume have been written by recognized authorities on the analysis, processing and utilization of important raw materials and products. As in other volumes of the series, the contents are quite heterogeneous. It is also obvious that there is not a complete coverage of all subjects in contemporary fat and oil industry in which there is major interest. Several other areas in which important advances have been made recently have been adequately covered in other publications, and are therefore not included here.

Volume 6 of the series, which is currently in preparation, will again deal with chemical and biochemical subjects.

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9 *September* 1957

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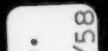

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STANDARD METHODS IN THE FAT AND OIL INDUSTRY

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STANDARD METHODS IN THE FAT AND OIL INDUSTRY

Virgil C. Mehlenbacher

I. Introduction

Analytical methods and physical tests are the tools by which most reactions and properties are measured. Such measurements are necessary for the proper evaluation of new products and new properties. They are obviously essential to scientific progress.

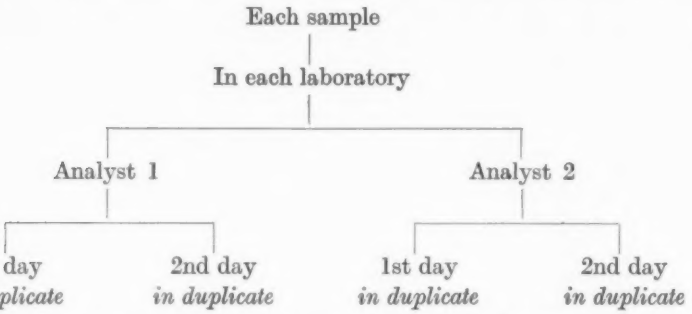
It is not an overstatement to say that a major development in fat and oil technology of the last quarter-century is the general improvement in methods of analysis. The time is well within recollection when the analyst had at his disposal methods for a few physical and chemical constants: procedures for moisture, impurities and unsaponifiable matter; and some miscellaneous tests of doubtful value. Today, the situation is different. Many of the older methods are no longer in use. Others have been improved and new ones have been added. Spectroscopy is well established. Dilatometry is proving a useful guide to formulation. Relatively new techniques such as adsorption analysis and counter-current distribution offer encouraging possibilities. These are but a few of the many techniques now used to provide more accurate and more significant information to the industry.

II. Standardization of Methods

Probably in no industry has more effort been directed toward the standardization and adoption of uniform analytical methods than the fat and oil industry. Several technical organizations support collaborative investigations leading toward the selection of adequate methods. The American Oil Chemists' Society, the Association of Official Agricultural Chemists, the American Society for Testing Materials, the Society for Analytical Chemistry, the Deutschen Gesellschaft, and the Fat Commission of the International Union of Pure and Applied Chemistry are the major groups that pursue the quest for stricter analytical methods.

The *modus operandi* for the selection and standardization of methods by the different organizations is similar. Samples are distributed to a group of co-operating laboratories with the method or methods to be studied and such specific directions as are necessary. The samples are analysed, and the resulting data are accumulated and processed with reference to the specific problem. In this way, it

is possible to determine with reasonable certainty the reliability of the method under investigation and the variations that may be expected within and between laboratories. A plan followed in some of the committee work of the American Oil Chemists' Society is to treat several samples individually as follows:



Laboratories should furnish all *individual* results including the individuals of duplicates.

From these data, may be determined:

(a) Precision within laboratories.
(b) Sources of within-laboratory variation.
(c) Precision between laboratories.
(d) Effect of levels on precision.

Data so acquired may be used to obtain a reliable estimate of variation. This sort of information is helpful to analytical chemists. In fact, these criteria largely determine the suitability of any method.

Table 1 lists some of the technical organizations that investigate and provide standard methods for industrial use. The group is not necessarily complete, but it does include those which are probably the best known. Many countries have adopted the methods of one or another of these associations. A very favourable situation is the close similarity of many of the methods. This is altogether as it should be, and it is hoped that eventually even greater uniformity will be attained.

III. Methods

A. Fat content

Most of the standard methods for determining the fat content of common source materials depend on the preferential solubility of fat and the insolubility of the non-fat substance in the same solvent. The general steps involved are:

(a) Preparation of the sample for easy removal of the fat.
(b) Extraction of the sample with a suitable solvent.
(c) Evaporation of the solvent followed by a gravimetric estimate of the residue.

Various forms of preparation are used, depending upon the substance to be analysed. Water is usually removed, or at least reduced to some relatively low level, and the particle size is reduced to a predetermined satisfactory size.

Caution is necessary to avoid overheating the sample during drying or grinding; otherwise, the solubility characteristics may be changed by oxidation. Care must be observed to avoid expression and possible loss of some of the fat. Some fat-containing substances, especially those which contain relatively large amounts of natural carbohydrate or protein, require a preliminary acid treatment to free the fat so that it will be totally extractable.

Table 1. *Method-standardizing organizations*

Organization	*Location*	*Methods*
American Oil Chemists' Society (AOCS)	Chicago, Ill., U.S.A.	Standardize and publish methods for fats and oils and allied products.
Association of Official Agricultural Chemists (AOAC)	Washington, D.C., U.S.A.	Standardize and publish methods. Includes section on fats and oils.
American Society for Testing Materials (ASTM)	Philadelphia, Pa., U.S.A.	Standardize and publish methods. Includes methods for a few oils.
Society for Analytical Chemistry	London, England	Standardize methods—publish in the *Analyst*. Some methods included in British Standard 684: 1950 published by British Standards Institution.
Fat Commission of the International Union of Pure and Applied Chemistry (IFC)	Paris, France	International group—standardize and publish methods for fats and oils.
Deutschen Gesellschaft für Fettwissenschaft e.V. (DGF)	Münster, Westf., Germany	Standardize and publish methods for fats and oils and allied products.

Ethyl and petroleum ethers are the common extraction solvents; however, there is an increasing tendency to use petroleum ether because it is more selective towards true triglycerides. Ethyl ether tends to give somewhat higher yields because of the solution of small amounts of non-fat substances. Combinations, such as alternate extraction with ethyl and petroleum ether, are used with some substances, particularly certain dairy products. Mixtures of alcohol and ether are employed to remove fat from certain biological materials, although this requires a subsequent treatment to eliminate the non-fat substances which are extracted by the alcohol. Treatment with alcohol facilitates the removal of fat from some materials.

The most efficient extractors for most source materials are the continuous percolator types such as specified by the methods of the American Oil Chemists' Society (1946). These are preferable to the conventional Soxhlet type. The Mojonnier extraction apparatus (Mojonnier and Troy, 1925) was originally intended specifically for dairy products, but it has been found to be

convenient for many other substances when it is desirable to make a liquid–liquid separation. This procedure utilizes a specially designed flask which permits an intimate mixture of fat and solvent, which is desirable in the removal of fat from a liquid phase. The Mojonnier flask is interchangeable with the Roese–Gottlieb flask specified in some methods for dairy products (ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1955a).

A recent idea to promote rapid extraction is to mix sample and solvent together in a high-speed comminuting device such as a Waring Blendor (HAMILTON and GILBERT, 1947). When this cutting device is operated at high speed, the particle size is rapidly reduced and the fat easily extracted.

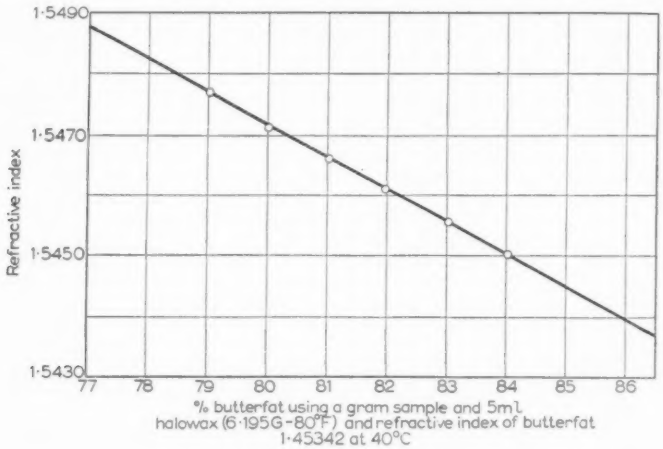


Fig. 1. Refractive index vs. % butterfat.

Various devices and techniques are employed if a rapid determination of the fat is desired. The addition of fat to an organic solvent brings about changes in several properties of the mixture which are proportional to the concentration of the fat. Density (SCHWARZ, 1930) and refractive index (INGRAHAM and SIMPSON, 1936; ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1955b) have been the most useful of these. In the case of refractive index, the sample and solvent are ground together in a mortar, filtered, and then the refractive index of the mixture is determined. The value obtained is referred to a previously prepared chart which relates refractive index to oil percentage (see Fig. 1). Density is similarly employed except that the portions of sample and solvent are generally much larger to meet the requirements of the apparatus. Standard density-measuring methods such as a hydrometer, pycnometer, or Westphal balance may be used for the density measurement.

A recent and promising development in methods of determination of fat is to measure the change in the dielectric properties of a specially selected solvent, brought about by the addition of fat. This method was originally developed for estimating the oil content of soybeans (HUNT *et al.*, 1952) and has since been

applied to linseed (HUNT *et al.*, 1953) and cottonseed (WHITTEN and HOLADAY, 1955). The procedure involves mixing sample and solvent together in a high-speed mill. The dielectric measurement is made on the resulting fat-containing solution, and the reading is then referred to a chart which relates dielectric readings with fat content. Undoubtedly, this technique is applicable to a wide variety of oil-bearing substances.

The conventional and historical method for determining fat in milk, cream and other dairy products is the Babcock test (ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1955a) (the Gerber test is the European equivalent). This procedure depends on digesting the sample with sulphuric acid in a specially designed flask. The fat liberated by the digestion ascends into a graduated neck during centrifuging and is measured volumetrically. This method, with various digesting reagents, has been applied satisfactorily to other fat-containing products such as comminuted meats (SALWIN *et al.*, 1955; OESTING and KAUFMAN, 1945). It is a useful, rapid and simple test although generally not as accurate or precise as the conventional extraction methods.

Table 2. Standard methods for oil or fat in various materials

Oil seeds	
Cottonseed, soybean, peanut, tung kernel, tung fruit, castor bean and flaxseed.	AOCS
Flaxseed.	AOAC
Coconut, shea, palm kernel, peanut, soybean, flaxseed, rape and sesame seed.	IFC
Oil seed by-products	
Cake, meal and meats; hull fibre; soya flour; castor pomace.	AOCS
Meat and meat products	AOAC
Cereal foods and dairy products	AOAC
Nuts and nut products	AOAC

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
AOAC. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS (1955) *Official Methods of Analysis*, 8th ed. Washington, D.C.
IFC. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.

B. Impurities

A concise and all-inclusive definition of impurities, applicable to natural fats and oils, is almost impossible. From one point of view, all non-glyceridic substances might be considered as impurities. However, natural fats contain many such constituents. Some non-fat substances such as unsaponifiable matter occur naturally; others, such as the free fatty acids are derived from glycerides; and still others, for example, moisture and soap, are foreign and are present because of contamination in transportation or processing. Probably the most distinctive feature of the list of impurities is that some or all of them are undesirable in one place or another and limitations on their presence appear in many trading specifications.

1. *Moisture*

The conventional methods for the determination of moisture in fats and oils can be classified into three groups, viz:

(a) Thermal drying—results include water and volatile matter.
(b) Distillation with an immiscible solvent—results represent water only.
(c) Titration with the Karl Fischer reagent—results represent water only.

The drying methods can again be divided into three types since the evaporation may be done under reduced pressure, in an air oven at atmospheric pressure, or over a hot surface such as a hot plate. Drying under reduced pressure is accurate so long as spattering does not result and providing no significant amount of volatile substance other than water is present. The same may be said for other drying methods, but the higher the temperature of drying the greater the likelihood of loss of non-aqueous volatile material. All natural fats contain volatile substances other than water, the amounts being variable and dependent on the grade of the fat. High-grade refined and deodorized vegetable oils contain only very small amounts, while dark tallows and greases may contain significant quantities. None of the drying methods is satisfactory for fats containing monoglycerides because these decompose rapidly under heat and yield an excessively high loss of volatile substances. In general, drying methods are not satisfactory if the water exceeds 1 per cent because of the difficulty in preventing spattering.

Distillation methods are applicable to almost all types of fatty materials providing there is no water-miscible substance present, and so long as the temperature of distillation does not exceed the decomposition point of some constituent of the sample. Distillation is not satisfactory for fats containing added monoglycerides. The distillation procedure involves distillation of the solvent from a mixture of solvent and sample. The water is removed with the solvent, condensed, and collected in a trap where it is measured volumetrically, while the solvent returns continuously to the distillation flask. Various organic solvents ranging from benzene to tetrachloroethane have been reported as satisfactory, but toluene and xylene are commonly used.

The Fischer volumetric method (1935) depends upon a reaction between water and a special reagent which is prepared from sulphur dioxide, iodine, pyridine, and methanol. The water-containing substance is suspended in methanol and titrated with the reagent which serves as its own indicator. The titration can also be performed electrometrically (Almy *et al.*, 1940) since there is a slight change in potential as the titration passes through the equivalence point. This method has been adapted to a wide variety of products. It has been combined with azeotropic distillation (Roberts and Levin, 1949) to determine micro quantities of water. For the specific determination of water, it is probably the best of all methods although it is not convenient for samples containing water is excess of 10 per cent because of the large amount of reagent required.

An excellent review of moisture methods was presented before the Analytical Division of the American Chemical Society during a Symposium for the

Determination of Water (STILLMAN, 1951). These papers deserve the attention of anyone concerned with this determination.

Table 3. *Standard methods for moisture*

Drying by vacuum, air oven, hot plate	AOCS
Drying by sand bath and gas burner	IFC
Drying by air oven	DGF
Distillation	AOCS
Distillation	IFC
Fischer volumetric	AOCS

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
IFC. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.
AOCS. DEUTSCHEN GESELLSCHAFT FÜR FETTWISSENSDRAFT E.V. (1950) *Einheitsmethoden*. Münster, Westf., Germany.

2. *Insoluble impurities*

The insoluble impurities usually consist of such foreign substances as meal, dirt and miscellaneous debris. The determination depends on the insolubility of these substances in organic solvents in which the fats are soluble. Kerosene and petroleum ether are specified in the method of the American Oil Chemists' Society, whereas the method of the International Fat Commission allows several solvents, the selection being dictated by custom or agreement.

Solvents for Insoluble Impurities:

(a) Kerosene, filtered, flash point (ASTM closed cup) 20°C min.
(b) Petroleum ether, AOCS specification H 2–41.
(c) Ethyl ether, neutral and freshly distilled.
(d) Light petroleum, b.p. 40–60°C—bromine index less than 1.
(e) Carbon disulphide, freshly distilled.

Table 4. *Solubilities of some impurities*

	Petroleum ether	*Ethyl ether*	*Kerosene*	*Carbon Disulphide*
Oxidized fats	Insoluble	Soluble	Insoluble	Soluble
Lime soaps	Insoluble	Insoluble	—	Soluble
Alkali soaps	Insoluble	Insoluble	—	Slightly soluble
Hydroxylated fats	Slightly soluble	—	—	—

Table 5. *Standard methods for insoluble impurities*

Impurities removed by filtration of kerosene solution of residue from moisture determination	AOCS
Impurities removed by filtration of solution of sample—not previously dried	IFC

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
IFC. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.

The type of solvent does not matter significantly so long as impurities other than meal and dirt are absent. However, if certain other materials are present, as they may be if the method is applied beyond the scope for which it was designed, the selection of solvent may be important.

3. *Acidity*

Acidity is expressed either as the percentage of free fatty acids or in terms of the number of milligrams of KOH required to neutralize 1 gram of sample (acid value). Numerically the acid value of ordinary fats and oils is approximately twice the percentage of free fatty acids. Acidity is determined by titration with standard alkali using either ethanol or *iso*propanol as a solvent for the fatty acids and soap. Since the glycerides are insoluble in ethyl alcohol, a two-phase system is always present during the titration. This is an inconvenience in observing the end point, especially if the acidity is low, but it need not detract significantly from the accuracy of the results. However, *iso*propanol eliminates this inconvenience because it readily dissolves fats. The sharpness of the end point may be improved by the addition of benzene or petroleum ether but this is not a common practice. Phenolphthalein is the usual indicator, although thymolphthalein and thymol blue are said to be somewhat better for dark-coloured samples. However, the titration can be done electrometrically and this is preferable when the colour change of phenolphthalein is indistinct.

Table 6. Standard methods for acidity

Colorimetric titration for ordinary fats and oils, fatty acids, drying oils and sulphonated oils	AOCS
Oxidized oils, lanolin and mineral acids	BSI
Electrometric titration	ASTM

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
BSI. British Standards Institution *British Standard* 684 : 1950. London, Eng.
ASTM. American Society for Testing Materials (1952) *A.S.T.M. Standards*, Philadelphia, Pa.

4. *Ash*

The ash content of animal and vegetable oils is extremely low except for the presence of such metals as may be present as contamination or purposely added in processing. The ash is determined by incinerating the sample until all organic matter is consumed. No special precautions are necessary except to avoid loss of the small amount of light and fluffy residue.

5. *Metals*

For the quantitative analysis of metals in fats, the sample is heated until completely ashed and all carbon removed. It is important that the temperature during incineration does not exceed 475°C; otherwise, some of the metals may be converted into non-recoverable forms. The ash, which should consist essentially of the oxides (or carbonates) of the metals, may be treated by any accepted procedures for the estimation of the metal or metals concerned.

6. *Sulphur*

Sulphur is not normally found in vegetable oils except as contamination, as in the case of carbon disulphide-extracted olive oil. A positive test is frequently found in some marine oils. There are two standard qualitative tests: (a) the coin test, and (b) the silver benzoate test, which is the more sensitive method. The coin test is simply a matter of heating the sample in contact with a polished silver coin. Sulphur is indicated by a discoloration on the surface of the coin. The benzoate test is performed by shaking a hot sample of the oil with a pinch of silver benzoate. The presence of sulphur is indicated by darkening of the mixture. Sulphur may be estimated quantitatively by oxidation of the sample in a Parr bomb followed by determination of barium sulphate.

Table 7. *Standard methods for sulphur*

Coin and benzoate tests	AOCS

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.

7. *Unsaponifiable matter*

Unsaponifiable matter includes those substances frequently found dissolved in fats and oils which cannot be saponified by the caustic alkalis but are soluble in the ordinary fat solvents. These include the higher aliphatic alcohols, sterols, pigments and hydrocarbons.

The common procedure for the determination is to saponify the sample with alcoholic alkali and remove the unsaponifiable fraction by extraction of the alcoholic soap solution. The extraction solvents are petroleum and ethyl ether. The former is satisfactory for most vegetable oils and tallows and greases. Ethyl ether tends to yield slightly higher results but, on the other hand, it also tends to promote the formation of stubborn emulsions during the extraction process. The method of the Society of Public Analysts (1933) specifies ethyl ether but the procedure is designed to minimize emulsification. This is undoubtedly the best method for marine oils or other oils of high unsaponifiable content.

Continuous extraction methods (Wood and Roschen, 1938; Rogers, 1939; Buerki and Holt, 1953) have not been successful, lacking accuracy and reproducibility. A more recent modification in which the soap solution is agitated continuously during extraction is claimed to correct the weaknesses of earlier procedures.

Table 8. *Standard methods for unsaponifiable matter*

Petroleum ether for ordinary fats and oils	AOCS
Ethyl ether for marine oils	AOCS
Petroleum or ethyl ether	IFC
Ethyl ether	BSI

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
IFC. International Union of Pure and Applied Chemistry (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.
BSI. British Standards Institution (1950) *British Standard* 684 : 1950, London, Eng.

8. *Petroleum hydrocarbons*

The presence of petroleum hydrocarbons or mineral oil in animal or vegetable oils may be due to contamination from processing or storage tanks or equipment, although petroleum distillates are used as denaturants, and solvents may be residual from an extraction process. Since hydrocarbons are unsaponifiable, it is not uncommon to attempt to estimate them from the unsaponifiable determination. To do this, one must assume some level for the natural unsaponifiable matter and attribute anything in excess of this to be due to petroleum fractions. There are two reasons why values so obtained are unreliable: First, even though the natural unsaponifiable matter is usually reasonably constant within certain limits, it nevertheless does vary from perfectly natural causes. Secondly, all of the hydrocarbon is not recoverable by this method of analysis; in fact, a great portion of it may be lost, especially if the mineral oil is one of the lighter grades. The loss occurs in evaporation of the solvent and drying of the residue. The loss on drying can be minimized by using a vacuum oven; however, it cannot be completely eliminated.

The British Standards Institution lists methods for determining water-insoluble solvents both lighter and heavier than water. These depend on removal of the solvent by steam distillation and collection in a graduated trap suitable for volumetric estimation. The AOAC Quantitative Method depends on separation of the hydrocarbon from the natural unsaponifiable matter by centrifugation in a medium of sulphuric acid. The hydrocarbon can also be separated from the unsaponifiable matter by adsorption analyses on an aluminium oxide column (Williams, 1949a). This is the most promising technique although it is not yet fully standardized, nor are the limitations altogether known.

Table 9. Standard methods for petroleum hydrocarbons

Solvents lighter or heavier than water	BSI
Qualitative and quantitative method for mineral oil	AOAC

BSI. British Standards Institution (1950) *British Standard* 684 : 1950, London, Eng.
AOAC. Association of Official Agricultural Chemists (1955) *Official Methods of Analysis*, 8th ed. Washington, D.C.

9. *Soap*

An accurate determination of soap in refined oil is more difficult than one might expect. The most common procedure is to ash 50–100 g and weigh the residue. An alternative method is to titrate the alkaline residue with standard acid after incineration. The alkalinity is then calculated as sodium oleate. A distinct disadvantage to either of these methods is that the light, fluffy character of the ash makes it difficult to prevent loss. Another disadvantage is that the small quantity involved approaches the limits of accuracy of the usual macro technique.

Several years ago, a committee of the American Oil Chemists' Society undertook and carried out a rather extensive collaborative investigation involving

several different methods. Unfortunately, this work did not result in the development or selection of a satisfactory procedure, although the Committee did indicate its preference (DURST, 1935; CRAPPLE, 1940).

Probably the best approach to the determination of soap is to estimate the positive ions such as sodium, calcium, iron or others. This can now be done quite rapidly and accurately by such techniques as emission spectroscopy (O'CONNOR *et al.*, 1947, 1948; MELVIN and HAWLEY, 1951) flame photometry, and colorimetric methods.

Table 10. *Standard method for soap*

Semi-quantitative determination	BSI

BSI. BRITISH STANDARDS INSTITUTION (1950) *British Standard* 684 : 1950, London, Eng.

10. *Chlorinated solvents*

Residual chlorinated solvent may be detected qualitatively by the common Beilstein test. In this procedure, a green colour results when a drop of the sample containing halides is heated on a copper wire in a Bunsen flame. SALLEE (1952) improved the sensitivity of the test for trichloroethylene by using a 40-mesh copper gauge, $\frac{1}{4}$ in. $\times$ 2 in. In another test ARNOLD and HALLOWEL (1947) adapted the Fujiwara reaction—adding two drops of sample to a hot mixture of sodium hydroxide and pyridine. EISDORFER and MEHLENBACHER (1951) remove the trichloroethylene from the sample by co-distillation with toluene and then treat the distillate according to the Fujiwara reaction (FUJIWARA 1914) to obtain a red colour which is measured in a spectrophotometer. This method will allow the accurate determination of as little as 0·001 per cent of trichloroethylene and is applicable to oil seed meal as well as oils.

Table 11. *Standard method for chlorinated solvents*

Detection of chlorinated solvents	AOCS

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.

11. *Methoxyl*

Methyl esters resulting from the use of sodium methoxide as a catalyst in the interesterification of lard may be determined with chromotropic acid (1,8-dihydroxynaphthaline-3,6-disulphonic acid). The sample is saponified, the methanol is recovered by distillation, oxidized with potassium permanganate and the product is then reacted with chromotropic acid. This method is reported to be sensitive to 0·0005 per cent methoxyl (ALLEN and BUSWELL, 1953).

C. Physical characteristics

Physical measurements of fats serve to provide considerable valuable information. They are useful for purposes of identification, for checking purity, and for the control of certain aspects of processing. Natural fats and oils of animal

and vegetable origin are rather complex mixtures consisting mainly of triglycerides with relatively small amounts of other components. Because they are mixtures, the melting and solidification temperatures are not sharp and definite as they are in pure organic compounds. Therefore, the terms 'melting' and 'solidification' do not carry the same significance as with pure substances of a definitely crystalline nature. Methods of measurement are empirical and the results depend on the conditions of the methods.

WILLIAMS (1941) employed a photoelectric device for determining the melting point. A beam of light is caused to pass through a small glass cell containing the samples and thence to a photoelectric cell which is connected to a galvanometer. Thus, the melting of the sample can be followed.

Another means of determining the melting point is from a dilatometric curve. (See the discussion on dilatometry.) Results obtained in this manner usually agree within a few degrees with the closed capillary tube melting points.

1. *Closed capillary tube melting point*

The closed capillary tube melting point of fats is determined in a manner similar to that commonly used for organic substances. A small portion of the sample is introduced into a thin-wall 1 mm glass tube sealed at one end. After solidification, the tubes containing the test portion are held at a low temperature for several hours, after which the tubes are gradually heated beside a thermometer in a water bath. The melting point is taken as that temperature at which the samples become completely clear.

2. *Wiley melting point*

A small disc of solid fat of definite dimensions is heated in an alcohol–water mixture until the disc assumes a spherical shape. The precision of this method between analysts (or laboratories) is not as good as the capillary tube procedure because the end point is less definite, and different people judge it differently. The results are not the same or necessarily close to those obtained with the capillary tube. The difference varies with the composition of the sample.

3. *Cold test*

The cold test is a standard requirement in the United States for vegetable oil sold as salad oil. The sample, contained in a 4 oz bottle, is immersed in a water bath maintained at 0°C. The oil must remain free from cloudiness and stearin crystals for $5\frac{1}{2}$ h.

4. *Flow test*

The flow test is used with neatsfoot oils, lard oils and similar products. It indicates the lowest temperature at which the oil will flow under the *arbitrary conditions* of the method. A sample contained in a test jar is cooled in a bath containing water, salt and ice until it is solid. It is then allowed to warm slowly until it will flow.

5. *Cloud point*

The cloud point is the temperature at which a cloud of stearin crystals of definite density forms as the sample is cooled and stirred. The method of the American Oil Chemists' Society is a manual operation; however, the end point may be measured by a photoelectric device.

6. *Congeal point*

The congeal, set and solidification points are similar; however, there is no standard method for any of these (COMMITTEE REPORT, 1945; BAILEY, 1956; DEUTSCHEN GESELLSCHAFT FUR FETTWISSENSDRAFT, 1950). A portion of the sample is cooled and stirred at a definite rate until solidification starts as indicated by a definite turbidity. Stirring and cooling is discontinued, and a thermometer is placed in the sample. The maximum temperature reached is the congeal point. Probably the greatest usefulness of such tests is in the control of plant processing as, for example, hydrogenation.

7. *Flow and drop points*

The procedure for determining flow and drop points is sometimes known as the Ubbelohde method (BRITISH STANDARDS INSTITUTION, 1940). The determination requires a special cup designed to hold the test portion of solid fat in juxtaposition to and surrounding the bulb of the thermometer. As the sample is warmed and softened, it flows downward through an orifice. The flow point is defined as the temperature at which the fat forms an approximately hemispherical protuberance at the orifice of the cup, and the drop point is the temperature at which the first drop falls from the cup.

8. *Slipping point*

The slipping point determination is applied to the sample without previous melting. The sample taken directly from the package is forced into a cylindrical brass cup which is suspended adjacent to a thermometer in a saturated salt solution. The bath is heated until the sample rises in the cylinder.

9. *Softening point*

The sample is prepared in the same manner as for the capillary tube melting point except that both ends of the tube are open. The end point is that temperature at which the test portion releases from the glass and starts to slide upward within the capillary tube. The results of this determination are extremely difficult to duplicate, and for this reason, if no other, its value is doubtful. This procedure is sometimes designated as the slip point or the open tube melting point.

10. *Refractive index*

The refractive index of a substance is the ratio of the speed of light in a vacuum to the speed of light in the substance. For practical measurements, the scales of standard instruments indicate refractive indices with respect to air

rather than to a vacuum. The refractive index is constant within certain limits for each type of oil or fat. It is therefore useful for identification. Since the refractive index is related to unsaturation, it correlates with the iodine value, however, the correlation differs for different types of oils. The determination of refractive index is very simple, requiring only a minute or two. For this reason and because of the correlation with unsaturation, the most important use of this property is in the control of hydrogenation.

11. *Smoke, flash, and fire points*

The smoke, flash and fire points are indications of thermal stability. In ordinary refined vegetable oils, the smoke point is dependent to a large extent on the free fatty acid content. Monoglycerides and diglycerides decompose at much lower temperatures than triglycerides and therefore lower the smoke point when added to natural fats. The flash point is used primarily to detect the presence of an excessive amount of low-boiling solvent such as may result from a solvent extraction process.

12. *Titre test*

The titre point is the temperature of solidification of the fatty acids of a fat. There are two standard methods for determining the titre point. According to the older procedure, the fat is saponified with an alcoholic solution of sodium hydroxide. The solidification point of the melted fatty acids is then obtained by an empirical procedure. This method has been largely replaced by the procedure of the American Oil Chemists' Society in which the saponifying reagent is potassium hydroxide in glycerol. Results from the two saponification procedures are not necessarily the same. The utility of this method is limited. It serves a purpose in evaluating fats for soap production, and it is useful for hydrogenated oils. Sometimes it is helpful in the identification of a fat.

Table 12. *Standard physical tests*

Closed capillary tube melting point	AOCS
Open capillary tube melting point	AOCS
Softening point	AOCS
Slip point	BSI
Slipping point	AOCS
Wiley melting point	AOCS
Cold test	AOCS
Flow test	AOCS
Cloud point	AOCS
Congeal point	DGF
Titre point	AOCS
Refractive index	AOCS, DGF, BSI, IFC
Flow and drop points	BSI
Smoke, flash and fire points	AOCS, DGF

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
DGF. Deutschen Gesellschaft für Fettwissensdraft e.V. (1950) *Einheitsmethoden*. Münster, Westf., Germany.
BSI. British Standards Institution (1950) *British Standard* 684 : 1950. London, Eng.
IFC. International Union of Pure and Applied Chemistry (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.

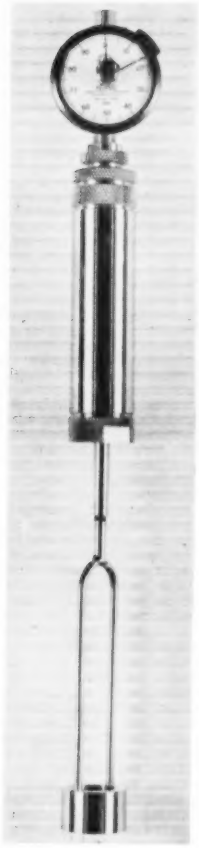


Fig. 2. Shortening consistometer

(*To face page 17*)

13. *Consistency*

Consistency is commonly expressed as a single value, athough it actually represents a combination of forces involving the yield value and viscosity (BAILEY, 1951b). Important as consistency is, there is no standard method for measuring or evaluating this property (RICH, 1942).

Essentially, all the methods that have been suggested depend on penetration. According to a micro penetration test suggested by FEUGE and BAILEY (1944) a small needle is allowed to drop freely into a small solidified test portion. The Bloom tester (CLARDY *et al.*, 1952) is a device which indicates the relative force that must be applied to force the plunger into the sample and, at the same time, force the fat through an opening in the end of the plunger (see Fig. 2). The force is indicated on a dial. An important advantage of this method is that it can be applied directly to packaged shortening so the consistency need not be disturbed by manipulation of the fat before the measurement is made. The ASTM grease penetration procedure (AMERICAN SOCIETY FOR TESTING MATERIALS, 1952) is probably the most common method. In this procedure, the consistency is indicated by the force necessary to force a cone of definite dimensions into the fat. A disadvantage of the method is that because of the construction and size of the apparatus, the sample must be removed from the original container before being tested. A possibility of error is thus introduced, since any working of the sample will change the apparent consistency.

The consistency of plastic fats varies with temperature and depends to a large extent on the relative amounts of liquid and solid fractions existing at any given temperature. Dilatometry provides a measure of the relative portions of liquid and solid fraction at any temperature and consequently is becoming increasingly significant as a means of controlling consistency (BAILEY, 1950; FULTON *et al.*, 1954; TEASDALE and SVARDAL, 1956).

14. *Viscosity*

The viscosity of fats and oils may be measured satisfactorily by any of the several standard methods devised for this purpose, providing that the selected procedure covers the necessary range. Most vegetable oils except castor oil have a Saybolt Viscosity of about 150–200 sec, at 100°F and 45–55 sec at 210°F. The viscosity of castor oils is much higher.

A capillary-type instrument is specified by the German methods for ordinary oils and the falling ball for bodied oils. The American Oil Chemists' Society requires the air-bubble procedure for high-viscosity samples using the Gardner–Holdt standards.

Table 13. *Standard methods for viscosity*

Drying oils—Gardner–Holdt	AOCS
Normal fats and oils—capillary tube	DGF
Bodied oils—falling ball	DGF

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
DGF. DEUTSCHEN GESELLSCHAFT FÜR FETTWISSENSDRAFT E.V. (1950) *Einheitsmethoden*. Münster, Westf., Germany.

15. *Colour*

The colour of animal and vegetable fats and oils is estimated in several ways, depending upon the country and the type of fat to be examined. (a) The Wesson method utilizing Lovibond colour glass and a Wesson comparator is used in the United States for most edible oils and fats. (b) The FAC method is designed for inedible fats, particularly tallows and greases. This method originated in the United States but its use has spread to many other countries. The FAC standards are a series of arbitrarily selected hues prepared from solutions of inorganic salts. (c) The Lovibond glasses and tintometer are used extensively in England and Canada. (d) The German Official Method specifies a solution of iodide as the colour standard, the comparison being made in a Pulfrich colorimeter. (e) The Gardner colour standards are specified by the Methods of the American Oil Chemists' Society and the American Society for Testing Materials for drying oils. The Gardner Standards are also solutions of inorganic salts.

A tentative procedure of the American Oil Chemists' Society provides for the determination of optical densities at several wavelengths. These values are used in an equation to calculate values which correlate with Lovibond colour reading. There are many shortcomings to this method—not the least of which is that results are correlated with purely arbitrary colour values. A recent and more logical approach to the problem of evaluating colour seems to be a quantitive estimation of those substances (pigments) responsible for colour.

All the methods mentioned depend on comparing the sample with some arbitrary standard. Furthermore, in almost all cases the comparison is visual and therefore highly subjective. There is a definite current opinion that methods involving arbitrary standards, visual comparison, and subjective measurements, should be replaced by more objective instrumental measurements. Considerable effort toward this goal has been made, however, the difficulties of transition have not yet been overcome altogether. This is particularly true because the methods are so deeply involved in trading rules and product specifications.

Table 14. *Standard methods for colour*

Wesson—Method using Lovibond glasses	AOCS
FAC standards	AOCS
Photoelectric method	AOCS
Iodine colour number	DGF
Gardner colour number	AOCS

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*. 2nd ed. Chicago, Ill.
DGF. Deutschen Gesellschaft für Fettwissensdraft e. V. (1950) *Einheitsmethoden*. Münster, Westf., Germany.

16. *Dilatometry*

Dilatometry is the systematic investigation of the variation in specific volume that occurs with change in temperature. In recent years, this technique has come to be extremely useful in characterizing certain fat mixtures and blends.

For examination, the sample is contained in a glass bulb to which is attached

a calibrated glass tube. The sample is confined under a fluid which may be mercury, an aqueous solution, or an immiscible organic liquid. The sample and container are maintained at a specified temperature until the volume remains constant and a volume reading is made. The sample and container are then raised or lowered in temperature, and then held until the volume again reaches a constant value before a volume reading is made. This is repeated at as many temperatures as desired.

When the volume is plotted versus temperature, a curve of the general form shown in Fig. 3 is obtained, the initial and final linear portions of the curve representing the completely solid and liquid states respectively.

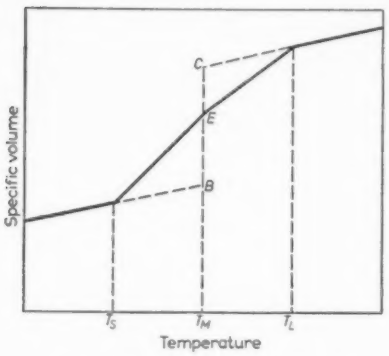


Fig. 3. Specific valve vs. temperature

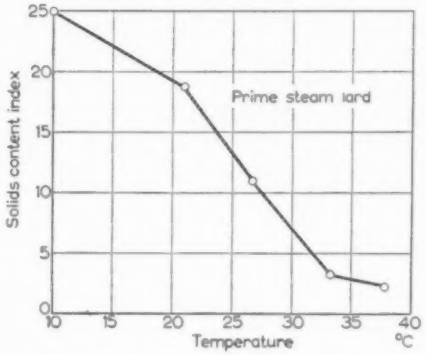


Fig. 4. Solids content index vs. temperature

The solid fraction at any temperature is represented by the fraction CE/CB and the liquid fraction is indicated by EB/CB. These values are actually only approximations; however, they are valuable for comparative purposes.

The percent solids measured in this manner may also be plotted as shown in Fig. 4. Such figures are easily obtained and are satisfactory for routine use. An exhaustive treatment of the use of dilatometry in fat chemistry has been made by Craig in *Progress in the Chemistry of Fats and Other Lipids*, Vol. 4.

D. Composition

1. *Polyunsaturated acids*

The most important advance in recent years in the analyses of fats has been in the measurement of fat composition. Probably no single method is more significant than the ultra-violet spectral procedure for estimating polyunsaturated fatty acids. This method is based on the fact that non-conjugated double bonds do not exhibit any special absorption characteristics in the ultra-violet; however, conjugated double bonds give rise to well defined maxima. The discovery that non-conjugated double bonds can be made to shift to a conjugated form by heating with alkali in glycol led to the formulation of a method for the quantitative estimation of linoleic and linolenic acids (Mitchell *et al.*, 1943). This has since developed into the current method of the American Oil Chemists'

SOCIETY (1946), which provides for the estimation of linoleic, linolenic and arachidonic acids. Oleic acid is calculated by subtracting the iodine value equivalent of the polyunsaturated acids from the total iodine value, and saturated acids are calculated by subtracting the sum of the unsaturated fatty acids from the total fatty acids.

There are several interesting and useful applications of ultra-violet spectroscopy at or near the stage of becoming standard methods, such as the determination of vitamin A (ASSOCIATION OF VITAMIN CHEMISTS, 1947) and the estimation of eleostearic acid (O'CONNOR *et al.*, 1953). It is not unlikely that new and additional techniques will appear which will add to the usefulness of this already invaluable analytical tool. For a detailed discussion of ultra-violet spectra of fats, the reader is referred to the chapter by Morton in *Progress in the Chemistry of Fats and Other Lipids*, Vol. 4.

O'CONNOR (1954) reports that during the period of 1900–1950, there appeared more than 100 technical papers dealing with the application of infra-red absorption spectrophotometry to problems in fat and oil chemistry. There are as yet no standard methods based on infra-red analysis; however, there have been some very important contributions. Probably the most significant of these is a method for the determination of *trans*-unsaturated acids in the presence of *cis*-unsaturated acids. (JACKSON and CALLEN, 1951). This is particularly important because of the lack of a satisfactory chemical method. For a full discussion of infra-red spectra of fats see Wheeler, in *Progress in the Chemistry of Fats and Other Lipids*, Vol. 2.)

2. *Saturated fatty acids*

The early methods for separation of saturated from unsaturated fatty acids were based on the insolubility of the lead soaps of the saturated acids in ether or alcohol. There are several variations of this method; however, in none of them is it possible to obtain a complete and sharp separation. The BERTRAM (1928) method depends on oxidation of the unsaturated acids with potassium permanganate. A fractional crystallization procedure, proposed by EARLE and MILNER (1940), was reported to be as good as other methods, at least on soybean oils. According to this method, the solid fractions are separated by crystallization from acetone at cold temperatures

Table 15. *Standard methods for fatty acid composition*

Ultra-violet absorption	AOCS
Saturated fatty acids	AOCS
From iodine and thiocyanogen values	ADES

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.

The saturated fatty acids in oils containing no acids more unsaturated than linoleic can be calculated from a combination of thiocyanogen and iodine

values. If acids more unsaturated than linoleic are present, this calculation procedure is not valid. Another similar method is based on a combination of iodine value and polysaturated acid determination by ultra-violet absorption. From these values, the saturated fatty acids may be calculated.

3. *Monoglycerides*

Polyhydric alcohols containing adjacent hydroxyl groups are oxidized by periodic acid or periodates in acid solution.

$$CH_2OHCH_2OH + 2H_5IO_6 \rightarrow 2HCHO + HIO_3 + 3H_2O$$

When the reaction is conducted at room temperature, the HIO_4 is reduced to HIO_3. If the reaction is allowed to proceed at elevated temperatures, the HIO_3 is further reduced and the formaldehyde converted to CO_2 and H_2O. This reaction is the basis for the quantitative estimation of monoglycerides. The method is performed by adding an excess of periodate reagent to the sample and then titrating the unreacted periodate with standard sodium thiosulphate. The amount of monoglyceride may be calculated from the quantity of periodate used. The determination of monoglyceride in fats is usually complicated by the presence of a small amount of free glycerin which must be removed before allowing the sample to react with the periodate.

It was long assumed that monoglycerides existed only as 1-monoglyceride: however, Brokaw, Perry and Lyman (1955) showed that commercial products may contain from 5 to 8 per cent as 2-monoglyceride. Accordingly, in a modified method the sample, after washing to remove glycerol, is treated with $HClO_4$ to isomerize the 2-monoglyceride. A periodate analysis is made before and after isomerization, from which 1- and 2-monoglyceride can be calculated.

4. *Hydroxyl groups* (Mehlenbacher, 1953)

In early terminology, OH groups were designated by the expression *Acetyl Value* or *Acetyl Number*, and the results were calculated on the weight of acetylated fat. This practice is now being discontinued. Acetyl value is being replaced by hydroxyl value, and the calculations are referred to weight of original unacetylated fat.

Hydroxyl groups in fats are determined by one of two methods: (a) acetylation with acetic anhydride followed by the determination of saponification values of acetylated and unacetylated portions, or (b) acetylation with an excess of acetic anhydride, hydrolysis of the excess anhydride, and titration of the acetic acid.

The first procedure is the Lewkowitsch method as modified by André and Cook. This procedure is widely used even though it is fraught with uncertainty. The second technique involving the use of acetic anhydride in pyridine is much simpler, and variations of this method have been applied to natural fats, monoglycerides and hydroxy-acids. However, there has been a tendency for results to be slightly low. The reason for this is not altogether clear. Probably the optimum conditions are not yet known.

The method of Ogg, Porter and Willits combines several desirable features of previous methods but it has not yet stood the critical test of wide usage. The recently adopted method of the International Fat Commission appears to minimize many of the shortcomings of earlier methods.

Table 16. *Standard methods for hydroxyl value*

Lewkowitsch, André, Cook procedure	AOCS, AOAC, BSI
Acetylation with acetic anhydride in pyridine	BSI, IFC

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
AOAC. Association of Official Agricultural Chemists (1955) *Official Methods of Analysis*, 8th ed. Washington, D.C.
BSI. British Standards Institution (1950) *British Standard* 684 : 1950, London, Eng.
IFC. International Union of Pure and Applied Chemistry (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.

5. *Neutral oil*

The constituents of natural crude vegetable oils are free fatty acids, pigments, phosphatides, neutral oil and certain resin-like substances. Of these, the constituent of prime concern, from a commercial point of view, is the neutral oil, i.e. the triglycerides.

Crude cottonseed and soybean oils and a few others of lesser commercial importance are traded in the United States according to the rules of certain trading associations who use the methods of the American Oil Chemists' Society for the purpose of evaluation. The most significant criteria are the refining loss, refined oil colour, and the refined and bleached oil colour. The method for refining loss was originally designed to indicate the oil recoverable by plant refining operations. Since the advent of the more efficient centrifugal refining equipment, the relation between laboratory loss and plant loss no longer exists. While the recovered oil is essentially neutral oil, the results in most cases are not comparable with the total available neutral oil.

There have been methods available for measuring total neutral oil (Wesson, 1926) for thirty years, but it is only recently that the determination has received much consideration and this, no doubt, is due to the inefficacy of the current methods of evaluation. Sylvester, Ainswerth, and Hughes (1945) showed that free fatty acid could be separated from neutral oil and unsaponifiable matter by absorption of the acids on a column of aluminium oxide. Linteris and Handschumaker (1950) adapted a similar procedure to the determination of neutral oil in crude vegetable oils. This method is now under investigation by a Committee of the American Oil Chemists' Society. Another approach to the estimation of neutral oil is to subtract the sum of the free fatty acids, insoluble impurities, moisture and phosphatides (acetone insoluble) from 100. However, the difficulties attending an accurate estimation of the substances classed as phosphatides throw doubt on the reliability of such a method of measuring neutral oil.

6. *Adsorption analysis*

Adsorption analysis and chromatography are discussed in detail in Vol. I of *Progress in the Chemistry of Fats and other Lipids*. There are only a few

analytical methods based on adsorption chromatography. A procedure for determining the neutral oil in crude vegetable oils, similar to the method reported by Linteris and Handschumaker, is being investigated by a Committee of the American Oil Chemists' Society. Butyric acid (KEENEY, 1956) can be quantitatively separated from butterfat by adsorption on aluminium oxide. WILLIAMS (1949b) has shown that the contamination of marine fats by fuel oil can be detected by adsorption analysis. KAUFMANN (1950, 1951, 1952) and his coworkers have reported an extensive investigation of the use of paper chromatography for analysis, identification and separation of fatty acids.

7. *Oxidized acids*

Oxidized fatty acids are characterized by their insolubility in petroleum ether. The British Standards Institution and IFC list a method for oxidized acids which is performed by saponification of the sample, release of the total fatty acids by acidification, and separation of the fatty acids with petroleum and ethyl ether.

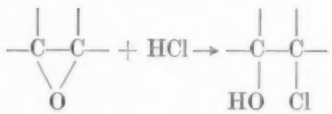
Table 17. *Standard methods for oxidized acid*

Applicable to soap stock	AOCS
Applicable to fats and oils	BSI, IFC

AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
BSI. BRITISH STANDARDS INSTITUTION (1950) *British Standard* 684 : 1950. London, Eng.
IFC. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.

8. *Epoxy groups*

The determination of epoxy groups has been well reviewed by JURGNICKEL *et al.* (1953). All of the methods for analysis of these compounds are based on cleavage of the oxirane ring with hydrochloric acid.



The general procedure involves allowing the sample to react with the acid in the presence of a solvent. The difference between the amount of acid added and the amount remaining after the reaction is a measure of the oxirane oxygen present.

9. *Micro methods*

Micro techniques are not commonly used in fat and oil analyses, although methods have been reported for most of the routine determinations made. Reference to several publications dealing with micro methods are listed below:

Micro saponification value, (1944) *Industr. Engng. Chem.* (*Anal.*) **16,** 410.
Fat constants, GORBACH G. (1940) *Fette u Seifen* **47,** 499.
Fat constants, KAUFMANN H. P. (1937) *Ber. Dtsch. Chem. Ges.* **70,** 2559.
Fat Extraction and fatty acid titration, DEWITT STETTEN, Jr. and GRAIL G. F. (1943) *Industr. Engng. Chem.* (*Anal.*) **15,** 300.

General, KRETCHMER N. (1948) *Amer. Oil Chem. Soc.* **25,** 404.
Micro penetration, FEUGE R. O. and BAILEY A. E. (1944) *Oil and Soap* **21,** 278.
General, SIMS R. P. A. and STONE B. *J. Amer. Oil Chem. Soc.* in press.

10. *Volatile fatty acids*

The volatile fatty acids are those low-molecular weight fatty acids that occur naturally in fats and which can be removed from hydrolysed fat by steam distillation. Butterfat and oils of the lauric acid group are characterized by the amount of these acids contained in them. Therefore, methods designed to measure the volatile fatty acids serve as indices of purity. The volatile fatty acids are of two types; those soluble in water and those insoluble in water. The soluble volatile acids as determined by the Reichert–Meissl Value are chiefly butyric and caproic, while the Polenske value is an index of insoluble volatile acids, mainly caprylic, capric and lauric. The Kirschner value is a measure of butyric. Another measure of low-molecular weight fatty acids, more common in Europe, is by means of A and B numbers. These depend on the solubility of the magnesium and silver salts. The A number is said to signify the amount of caproic, caprylic and capric acids while the B value is an indication of butyric acid. These methods are highly empirical, and the specifications of procedure and apparatus must be followed in detail if results are to have any relation one to another (ZEHREN and JACKSON, 1956).

A relatively new procedure for separating and measuring the individual fatty acids by adsorption analysis appears to be a far more reliable measure. This method has been successfully used as a means of detecting the adulteration of butterfat in ice cream (KEENEY, 1956).

Table 18. *Standard methods for volatile fatty acids*

Reichert–Meissl value	BSI, AOCS, IFC
Polenske value	AOCS
Kirschner value	BSI, AOCS
A and B numbers	IFC

BSI. BRITISH STANDARDS INSTITUTION (1950) *British Standard* 684 : 1950. London, Eng.
AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
IFC. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (1954) *Standard Methods for the Analysis of Oils and Fats*. Paris, France.

E. Chemical characteristics

Certain of the chemical reactions of fats, especially those associated with hydrolysis and unsaturation, form the basis for a few common and important analytical tools. The principal determinations are:

Iodine value—measure of total unsaturation of fats containing non-conjugated double bonds.
Diene value—measure of conjugated unsaturated bonds.
Hydrogen value—measure of total unsaturation.
SCN value—Dependent on unsaturation—in combination with iodine value permits calculation of fatty acid composition.
Saponification value—measure of molecular weight.

The values listed above are frequently termed fat constants, for the reason that each is constant within certain limits for each type of oil. They aid in identification; they are helpful criteria in assessing purity; and they are important considerations in certain processing operations as, for example, soap making (saponification value) and hydrogenation (iodine value).

1. *Iodine value*

The iodine value is based on the absorption of halogen at the unsaturated bonds. There are several methods for determining the iodine value but the most important are the Wijs (1898) and the Hanus (1901). The Wijs method is probably the most widely used and it is believed to yield results closer to theoretical values than any other method. Hanus results range from 2 to 5 per cent below Wijs, but the Hanus reagent has the advantage of being quite stable. A few of the other methods include the Margosches (Margosches *et al.*, 1924), Hubl (1884), Kaufmann (1926), and the Rosenmund and Kuhnhenn (1923). These have not been accepted, largely because of erratic results, although there are some special cases where the Rosenmund–Kuhnhenn method is said to be preferable. Under the usual conditions the adsorption of halogen by conjugated double bonds does not proceed to completion in a reasonable time, so that this reaction is not satisfactory for fats such as tung oil. A recent modification of the Rosenmund–Kuhnhenn method is reported to overcome this difficulty. (Planck *et al.*, 1953).

2. *Hydrogen value*

Hydrogenation is becoming an important analytical procedure to measure unsaturation in fats containing conjugated double bonds. Although such fats do not absorb halogen readily, there seems to be no hindrance or inhibition to the addition of hydrogen. The hydrogen value depends on the absorption of hydrogen at the unsaturated bond. The reaction takes place when the sample, containing a catalyst such as nickel, palladium or platinum, is heated in the presence of hydrogen gas. The volume of hydrogen absorbed is determined from measurements before and after the reaction and reduced to standard conditions. The hydrogen value, sometimes called the hydrogen iodine value, is calculated in terms of its iodine equivalent. There is as yet no standard method for this determination; however, there have been several publications indicating progress in the development of a suitable technique (Pack and Planck, 1953).

3. *Diene value*

The diene value is a measure of the conjugation of unsaturated double bonds. The method depends on the Diels–Alder reaction between maleic anhydride and conjugated double bonds (American Oil Chemists' Society, 1946). An excess of maleic anhydride is added to the sample and the mixture is heated. Water is added to hydrolyse the excess reagent, and the resulting acid is then titrated with standard alkali. The determination is empirical and the method

must be closely followed; also, it is subject to interference from certain substances, chiefly oxidation products. A new procedure is under investigation by a Committee of the American Oil Chemists' Society, which depends on ultraviolet spectrophotometric absorption.

4. *Thiocyanogen value*

The thiocyanogen value is determined in a manner similar to the iodine value, and results are reported in terms of equivalent amounts of iodine. The addition of SCN to polyunsaturated bonds differs from the addition of halogen in the amount added at the various double bonds. Formerly, it was thought that SCN added quantitatively to one of two double bonds of a non-conjugated diunsaturated acid and at two of three double bonds of a triunsaturated acid. It has since been shown that the extent of the addition is variable depending on time, concentration, and other conditions of the reaction. However, by careful standardization of the method, the results are reproducible. The value of this method is that in combination with the iodine value, it allows calculation of fatty acid composition for some fats.

5. *Saponification value* (HALL and SHAEFER, 1954)

The saponification value is a measure of the amount of alkali required to saponify a definite weight of fat. It is also an indication of the average molecular weight of the fat. This procedure was originated by Koettsdorfer and it is sometimes known by this name. The procedure involves heating the sample with an excess of alcoholic KOH followed by back titration of the excess alkali with standard acid. While both the reaction and procedure appear to be relatively simple, this is not altogether true because results are not always reproducible. The reasons are not clear but two important points to watch during the determination are (a) to avoid any loss during saponification, and (b) to make sure the reaction is continued to completion.

Table 19. *Standard methods for chemical characteristics*

Iodine value—Wijs	AOAC, AOCS, BSI, IFC, DGF
—Hanus	AOAC, DGF, IFC
—Hubl	IFC
—Kauffman	DGF
Thiocyanogen Value	AOCS, AOAC, DGF, IFC
Diene Value	AOCS
Saponification Value	AOAC, AOCS, BSI, IFC, DGF

AOAC. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS (1955) *Official Methods of Analysis*, 8th ed. Washington, D.C.
AOCS. AMERICAN OIL CHEMISTS' SOCIETY (1946) *Official and Tentative Methods*, 2nd ed. Chicago, Ill.
IFC. INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY (1954) *Standard Methods for the Analysis of Oils and Fats*. Paris, France.
DGF. DEUTSCHEN GESELLSCHAFT FÜR FETTWISSENSCDRAFT E.V. (1950) *Einheitsmethoden*. Münster, Westf. Germany.

F. Identification

Unfortunately, there is no organized scheme for the qualitative analysis of fats and the problem of identification of individual fats and oils is not a simple one.

This is particularly true in the case of mixtures and processed fats. In fact, it is quite possible to encounter mixtures which practically defy identification of the original individual constituents.

There are a few tests which are specific for certain individual oils or small groups (WILLIAMS, 1950), but in many cases the specific reaction is destroyed by processing. A typical example is the Halphen test for cottonseed oil. Another aid to identification is to determine the chemical and physical characteristics of the sample and compare the values obtained with comparable values of samples of known purity. This is usually a fruitful procedure when the unknown consists of a single oil or fat. It may even be helpful in the case of a mixture of two fats, but beyond this the task becomes quite difficult.

When identification is necessary, recourse is usually sought in the following: (a) specific tests which give characteristic reactions with certain oils or fats, (b) physical and chemical constants such as saponification value, iodine value, titre point, and others which are constant within certain limits for individual fats and oils, and (c) determination of fatty acid composition.

G. Stability (LEA, 1938)

Fat stability tests are designed to measure resistance to oxidation, which is the most common cause of fat deterioration. There are three types of methods used for the estimation of fat stability.

(a) *The Schaal test* (POOL, 1931) involves incubation of the sample at some temperature such as 60°C. The odour of the sample is observed periodically until rancidity is detected. This method is entirely subjective and therefore likely to lead to results of considerable variation.

(b) *Oxygen absorption* (ECKEY, 1946). The sample is heated in the presence of oxygen until the rate of absorption of oxygen undergoes a definite increase. This method has the advantage of being a direct measure and does not depend on the rate of formation of decomposition products.

(c) *The active oxygen method* (KING *et al.*, 1933; MEHLENBACHER, 1942). The fat is heated and air is blown through it at a controlled rate until the peroxide content increases to some level which has previously been shown to coincide with the onset of rancidity. The AOM procedure is widely used throughout the industry however, it is not uncommon for results to vary considerably, especially between laboratories.

The peroxide content serves as an indicator of the level to which oxidation has proceeded. This method provides a means of ascertaining the freshness of fats, particularly in the early stages of oxidation. The determination of peroxides is extremely empirical, however, depending on the method and conditions. Almost any variation in procedure or technique may lead to variation in results. Carbonyl groups are also formed during oxidation; however, these are more difficult to determine and their rate of development is similar to the rate of development of peroxides.

There are no official methods for fat stability but the peroxide value determination has been standardized by several associations.

Table 20. Standard methods for peroxide value

Peroxide value	BSI, AOCS, IFC

AOCS. American Oil Chemists' Society (1946) *Official and Tentative Methods*, 2nd ed. Chicago Ill.
BSI. British Standards Institution (1950) *British Standard* 684: 1950, London, Eng.
IFC. International Union of Pure and Applied Chemistry (1954) *Standard Methods for the Analysis of Oils and Fats*, Paris, France.

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2

MONSAVON CONTINUOUS PROCESS FOR SOAP MANUFACTURE

F. Lachampt and R. Perron

Monsavon–l'Oreal, Usine de Clichy, France

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2

MONSAVON CONTINUOUS PROCESS FOR SOAP MANUFACTURE

F. Lachampt and R. Perron

THIS process which applies particularly to the findings of McBain and his school on the washing of soap, and those of one of us on saponification, forms the subject of French patents 946741–42, 946746 and 989596. It accomplishes continuously saponification, counter-current washing and fitting.

In the following account the principles of these operations are described and their effective application in the process examined by means of a general diagram of the installation, supplemented later by such detail as is required in the development of the subject. Next, directions are given concerning control of the plant and the method of arriving at balances and yields. In conclusion, other matters are considered, such as the advantages of continuity, the flexibility of the process, the raw material changes possible and the purity of the soap.

I. PRINCIPLES OF THE CHEMICAL OR PHYSICOCHEMICAL OPERATIONS

A. Saponification

This is an exothermic reaction initiated by a caustic lye, which is manifest as the simultaneous hydrolysis of the glycerides and the neutralization of the free acids thus liberated. It is essential to recognize that the initial reactants, glycerides and caustic lye, are not miscible. It is first necessary, therefore, in order to obtain the rapid reaction favourable to a continuous process, to create an intimate mixture of these reactants. This can be done in two ways, the use of a solvent or the promotion of a fine emulsion. In the Monsavon process the latter method is adopted.

Moreover, the soap formed contributes, by reason of its amphiphathic nature, to the degree of dispersion proportionate to the degree of saponification, and consequently to the rate of reaction. The middle phase of soaps should be minimized because it is very viscous and difficult to handle. Also, the saponification should terminate in the production of neat soap. This can be achieved by the introduction of salt during the course of saponification, or by preserving, during the reaction, a concentration of electrolyte which is always sufficient to avoid the middle phase.

These last considerations suggest operating with a concentrated caustic lye

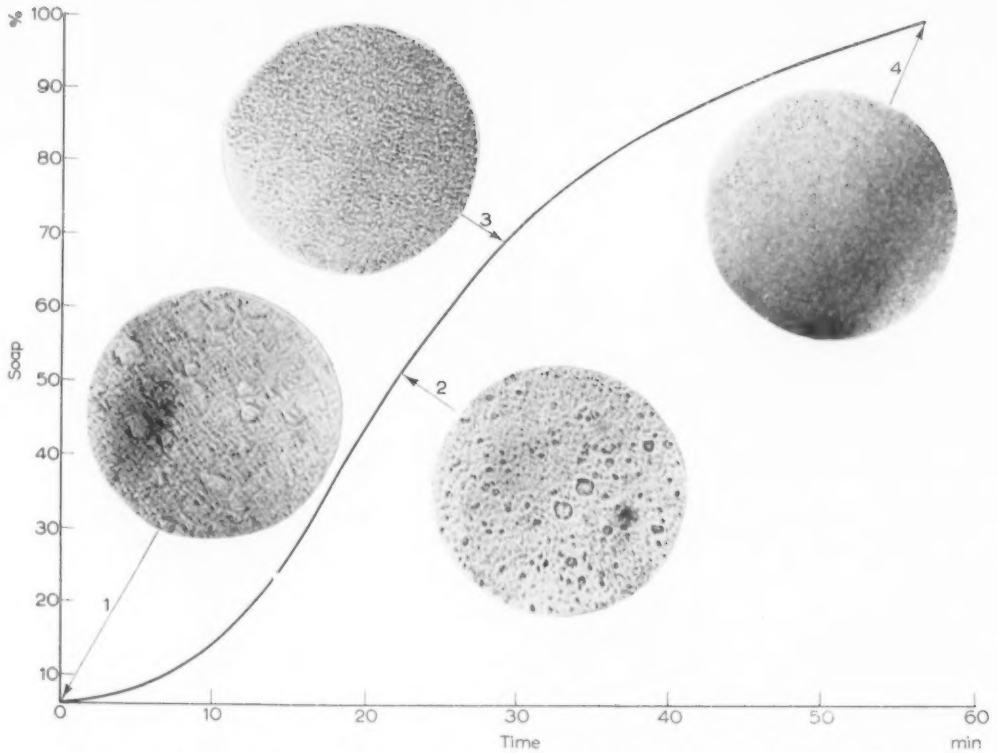

Fig. 1. Curve illustrating saponification of water-in-oil emulsion (magnification = 590×). Emulsion hand-stirred; temperature 45°C; caustic soda 35%. 1—emulsion at commencement (erystallized); 2—48·5% soap; 3—66·3% soap; 4—completion.

(To face page 32)

Fig. 2. Diffusion of caustic soda through the soap.

which allows the reaction to proceed direct to the neat phase without the addition of salt. This governs the initial state of emulsion which must therefore always be of the water-in-oil type (LACHAMPT, 1945).

This being so, the evolution of the physical state of the emulsion in the course of saponification and the mechanism of this reaction are as follows. First the reaction establishes itself as autocatalytic, that is to say, that the soap formed accelerates its own formative reaction. The reaction can be split into three stages: the first being slow, the second rapid and the third again slow, as shown by the curve in Fig. 1. Initially, the emulsion formed from the fat and the soda lye is sufficiently fluid, if the fat does not contain free acid, the immediate transformation of which into soap during the emulsification accelerates the saponification. The microscopic appearance shows a mobile mass composed of small sacs of alkali with a reasonably rigid external interfacial layer, floating in the oil.

When saponification takes place, the thickness of these sacs is increased and at the same time there is a diffusion of alkali through the layer of soap formed, to reach the triglyceride to saponify it. The mass therefore acquires a rigidity which departs when saponification is complete. At this point, there is no longer an excess of alkali (if the calculated requirement has been used) and the fluid neat-soap stage is attained. The saponification is practically instantaneous at the interface. The micrographs in Fig. 1 show four successive states of the mass. Fig. 2, taken from a previous publication (LACHAMPT *et al.*, 1947) shows the diffusion of the alkali through the soap to the glyceride. In the work quoted it was shown that as the saponification approaches a constant rate, so the solution pressure of the soda also becomes constant, the rate of propagation being independent of the area of the interface.

It is important not to agitate after having formed the emulsion and when the saponification commences. In fact, by agitation, the rigid walls of the sacs are broken and the emulsion cannot re-establish itself. The initial presence of free fatty acids in the fat leads to the immediate formation of soap and the rigidity becomes immediately apparent. There is then a risk of a stoppage during the preparation of the emulsion.

F. LACHAMPT *et al.* (1947) studied the influence of various factors on the saponification. His findings were as follows:

1. *Influence of dispersion.* With a tallow (45°C) and a 35 per cent caustic soda lye in slight excess, the fineness of the emulsion was varied by preparing it in four different ways for 3 min: by hand, by kitchen whisk, by Moritz turbo-agitator and with a Premier homogenizer. The results as shown by the curves in Fig. 3 indicated that the finer the emulsion is, the more rapid the reaction.

2. *Influence of the temperature during emulsification.* Fig. 4 shows the effect on saponification of forming emulsions of different degrees of dispersion at 55°C as compared with 70°C.

At these temperatures the reaction commences normally but slackens off suddenly or stops ('breaking'). The emulsion breaks because the temperature

of the fat is too high at the time of emulsification. Fig. 5 illustrates this aspect for a hand-made emulsion at 55°C at the instant of most characteristic appearance.

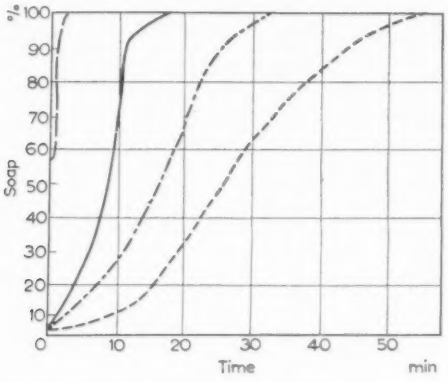

Fig. 3. Influence of the initial degree of fineness of emulsion on saponification. Caustic soda 35%; temperature of tallow 45°C; S. V. of tallow 194; F. F. A. of tallow 1·9%.
– – – – hand-stirred emulsion — — — — Premier mill
— — — — whisked emulsion ——— Moritz turbo-agitator

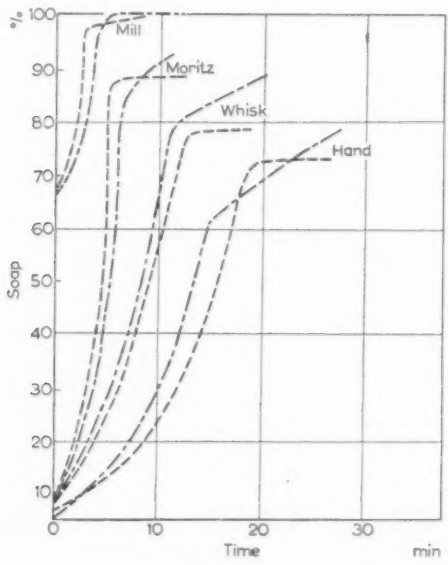

Fig. 4. Influence of temperature of emulsification on saponification.
— — — — temperature 70°C — — — — temperature 55°C

3. *Influence of the concentration of the soda lye.* The curves in Figs. 6 and 7 represent the results obtained at 45°C with 25 and 30 per cent caustic lyes for different finenesses of emulsion. It is not possible, generally, to obtain a hand

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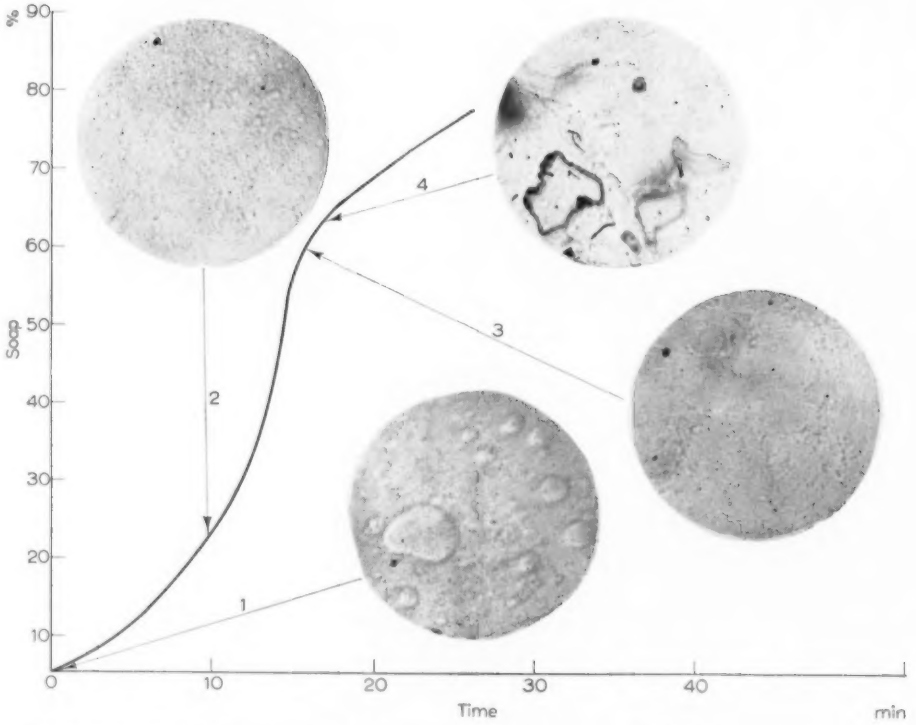

Fig. 5. Curve illustrating saponification of a water-in-oil emulsion, with 'breaking' due to too high an emulsification temperature. Emulsion hand-stirred; temperature 55°C; caustic soda 35%. 1—initial emulsion; 2—21·5% soap; 3—start of 'breaking' at 61·5% soap; 4—broken emulsion at 64% soap.

(To face page 34)

emulsion with 25 per cent caustic and where one is formed it is not stable at 100°C. For the other emulsions the reaction commences normally but is stopped by 'breaking'. With 30 per cent soda, some saponifications are self-terminating and others diminish considerably in reaction rate because of breakage of emulsion. Curiously enough, the coarse emulsions terminate reaction without showing interruption of the curve.

4. *Influence of the fatty acids and catalysts.* If the fat contains free acids initially, the emulsions are apparently more stable and the saponifications are

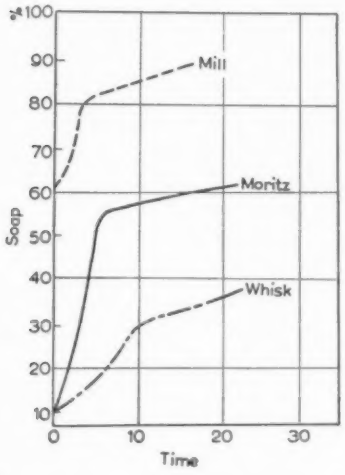

Fig. 6. Influence of concentration of caustic soda on saponification. Temperature 45°C; caustic soda 25%.

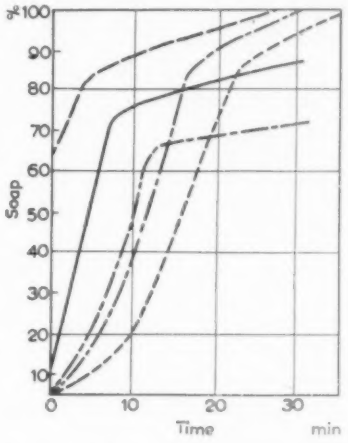

Fig. 7. Influence of concentration of caustic soda on saponification. Temperature 45°C; caustic soda 30%.
– – – hand-stirred emulsion
— — Premier mill
— – — – whisked emulsion
—— Moritz turbo-agitator

rapid and self-terminating even with a 30 per cent lye, whilst with a 25 per cent lye 'breaking' again occurs, but with an advanced degree of saponification.

The presence of certain catalysts, e.g. β-naphthol, is found to complete saponifications which would be incomplete in their absence.

B. Washing of soap

This operation can be explained and understood only by a phase diagram. Reference is therefore made to the practical ternary diagram, soap*–water–salt, reproduced on Fig. 8 from the work of Loury (1955).

It should be remembered that this diagram refers to equilibrium states for a constant temperature (90°C). The table adjoining the diagram indicates the co-ordinates of the various characteristics for charges of tallow and coconut oil and mixtures of the two.

In this diagram an ideal soap is represented by point H. It is a soap containing a little salt. To obtain such a soap it is necessary, in washing the crude

* Expressed as the corresponding fatty acids.

soap with brine, to adhere to the line EH, the triangle CEH being that of the invariant, neat-soap–isotropic solution–lye.

This situation can be attained in three ways:

(a) It is known that all the slopes terminating in neat soap converge towards a theoretical soap in the neighbourhood of 66 per cent fatty acids which can be

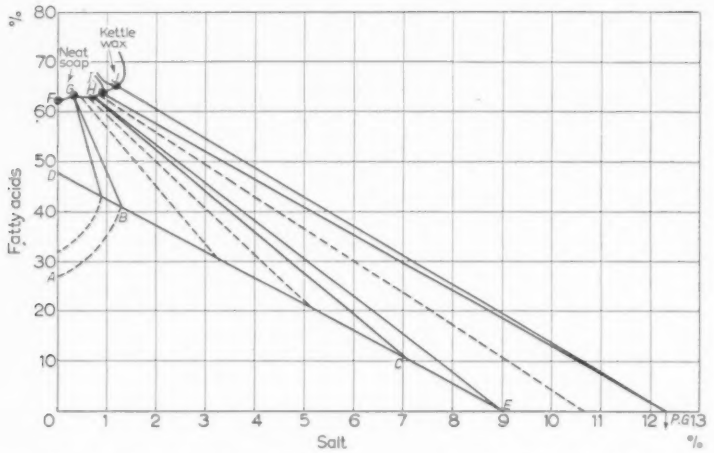

Fig. 8. Ternary diagram at 90°C for a soap processed from 25% copra and 75% tallow.

	Tallow		*Copra*: 25% *Tallow*: 75%		*Copra*: 75% *Tallow*: 25%		*Copra*	
	Fatty acids (%)	*NaCl* (%)	*Fatty acids* (%)	*NaCl* (%)	*Fatty acids* (%)	*NaCl* (%)	*Fatty acids* (%)	*NaCl* (%)
A	23	0	27	0	33	0	35	0
B	38	1	41	1·3	44	2·6	45	3·4
C	11	5·1	11	7	11·5	12·5	12	18
D	43	0	47·5	0	52	0	53	0
E	0	6·8	0	9	0	16·2	0	23
F	62	0	62	0	62	0	62	0
G	63	0·2	63	0·3	63	0·5	63	0·6
H	63	0·5	63	0·7	63	1	63	1·6
I	63·5	0·65	63·5	0·9	63·5	1·3	63·5	2
J	65	1	65	1·2	66	1·5	67	2·2
PG	0	9·5	0	12·3	0	19·8	0	29

considered to be pure neat soap. This being so, a saponification leading to a 66 per cent fatty acid, electrolyte-free soap, can be envisaged, whereby the extension of the line EH is located.

(b) A saponification can be effected leading to a soap with 63 per cent fatty acids and 0·2 per cent NaOH (electrolytically equal to 0·22 per cent of salt). This gives point G, and it is then only necessary to adjust with a lye more concentrated than the limit-lye so as to fall on EH.

(c) One can adjust directly with saturated brine to attain EH and wash subsequently with limit-lye.

The last method has been found preferable. In fact, if the 66 per cent fatty acid soap is feasible, it should swell. Therefore it is thick and flows badly with the result that it is difficult to establish equilibrium with the lye, although it can be said that this method works in practice. The second means has been discarded in principle, in the Monsavon process, because it entails, by the arrangement adopted, a salt concentration in the whole apparatus always greater than the limit-lye. Control is thenceforward very poor, settling is imperfect and the soap always retains lye. The third method is more convenient as it lends itself to a rigorous control by the limit-lye.

These considerations will moreover be more clearly appreciated after the description of the process itself.

This examination of the conditions of washing of the soap brings out clearly the importance of Merklen's concept of the limit-lye (Merklen, 1906). Nevertheless, if it is easy to show its function on the laboratory scale, notably for settlement and for working in jacketed vessels, it is necessary, however, in industry to consider other intervening factors, particularly gases occluded by the fats and agitation.

It should be remembered that the washing of soap has two objects: recovery of glycerol and removal of impurities. Washing with limit-lye permits these to be attained, giving a good recovery of glycerol and using at the same time that concentration of salt which is conducive to removal of impurities.

C. Fitting

This operation consists essentially of the addition to the washed soap located on EH, of water or lye less concentrated than limit so as to enter the region 'neat soap–isotropic solution', that is to say to lead to a finished soap settled between G and H. It is necessary, however, to endeavour to have a soap having composition as near as possible to H, where the neat soap has maximum fluidity, and a 'nigre' (isotropic solution) as low as possible in soap. This entails rapid fitting.

This leads to the ultimate requirement of location near C. As is shown by Fig. 8, by addition of water alone, control is very difficult, these additions being very small. Also, one would have, at the end of the operation, a neat soap in equilibrium with a too-rich nigre. On the other hand, with water containing electrolyte a little below the concentration of limit-lye the additions become sufficiently large to permit easy control.

Regarding these considerations of principles and concerning soap generally, the reader could usefully consult Lachampt and Perron (1953).

II. Description of Plant

In this description, the principles expounded above will be examined with regard to their practical application in the three operations of soap manufacture, saponification, washing and fitting, which form three distinct departments in the installation.

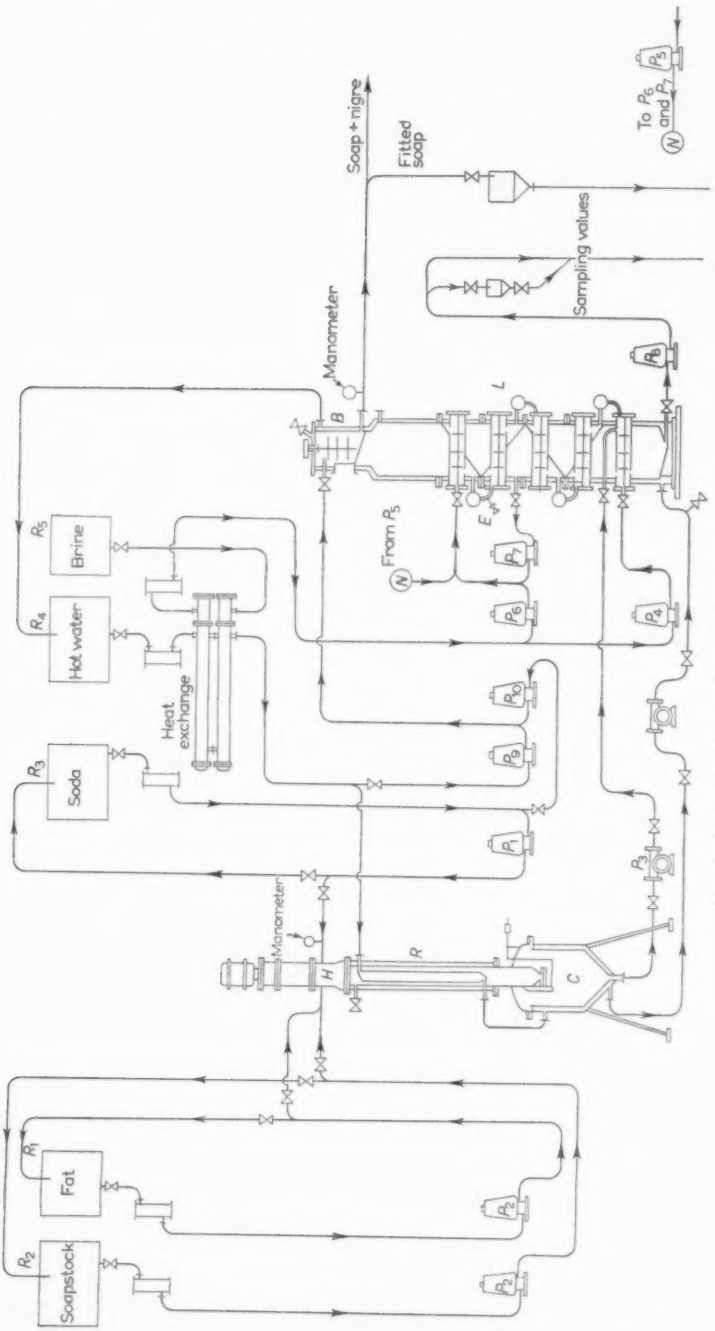

Fig. 9. Schematic diagram of the Monsavon process.

Description of Plant

The general scheme of the Monsavon plant to which we refer is shown in Fig. 9.

Raw material feed is provided for, in the case of fat, by two constant-level reservoirs Rl and R2 and, in the case of reagents, by three constant-level reservoirs R3, R4, and R5, respectively supplying caustic soda lye, hot water and brine.

All fluids are transported by volumetric pumps and, excepting the soda lye, are pre-heated before entering the apparatus. The brine is pre-heated in a heat exchanger by the circulating water. The whole installation is in hot-water jackets maintained at constant temperature, usually 85–90°C, to ensure that the operations are carried out in conditions corresponding to those shown in the phase diagram (Fig. 8) established for this determined temperature and representing the equilibria relevant to it. In order to facilitate delivery about the plant and re-starting, the pumps and pipelines carrying the fat, soap and nigre are steam-jacketed.

A. Saponification

This is carried out in the conditions necessary for obtaining predictable results. It is preceded by emulsification of the fat with the soda lye. The saponification section of the plant comprises essentially a homogenizer H, a reactor R and a crude soap vat C.

1. *Homogenizer.* The concentrated soda lye, at ordinary temperature, suitable for production of a crude soap having a neat phase situated at the lower limit, that is to say about 63 per cent fatty acids, the position of maximum fluidity, and the fats, more or less heated according to their acidity, are brought by the saponification volumetric pumps, P1 and group P2, to the top of the homogenizer. The temperature at which the reactants are fed in is so chosen that the heat of the saponification reaction raises the temperature to at least 103°C, the boiling point of the aqueous phase of the solution in the neat phase. The fat supply is controlled by the group of pumps P2 according to the nature of the stock and production capacity of the apparatus, and the caustic lye is controlled by P1, according to the saponification value of the fat used and the concentration of the lye. The quantity of caustic is so arranged as to give a soap containing 0·2 per cent free alkali.

The emulsion is formed in two stages; first, in a mixer then in the homogenizer proper; these two vessels together constitute the homogenizer H, shown in detail in Fig. 10.

The mixer, the purpose of which is to prepare a primary emulsion, consists of two coaxial perforated cylinders, one fixed, one mobile, sufficiently close to one another. The fat and the caustic lye are fed into the upper compartment, and traverse this region forming a coarse emulsion which is carried by a helical impeller to the lower compartment and forced by the impeller into the Premier homogenizing mill. Mixer and homogenizer are carried on the same shaft driven at about 3,000 r.p.m. The gap of the Premier mill is adjustable.

2. *Reactor.* The fine emulsion formed in the above process passes into the reactor R. This is a cylindrical tube heated by the general hot-water circulation

which passes through two sheaths, one external and one internal. In contact with the hot walls saponification commences. The tube must always be kept full and under slight pressure to avoid entry of air into the emulsion. At the base of the reactor there is a retaining valve governed by a counterweight.

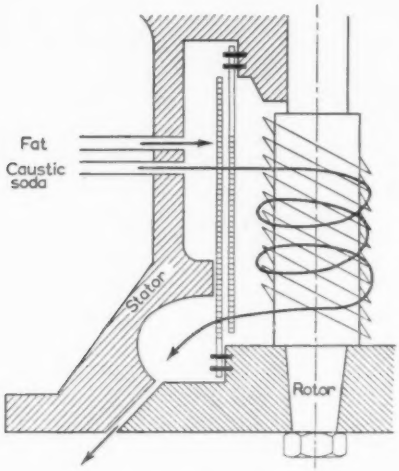

Fig. 10. Homogenizer.

3. *Crude soap vat.* From the tube the soap flows into the crude soap vat C, where it remains for about ½ h. A constant level is maintained in this vat by means of the regulated soap pump P3. Its capacity is approximately 1 ton of soap.

B. Washing

The soap is delivered by the pump P3 to the washing tower L. This may comprise five, six or eight washing stages and is surmounted by a 'fitting box'. This, like the rest of the apparatus, is surrounded by a hot-water jacket. The latter is to permit operation within the ternary diagram and to give flexibility to the installation which can thus be stopped and re-started without special precautions.

The washing is counter-current, the soap arriving at the first stage at the base of the tower and emerging from the fitting box whilst the brine and nigre are led to the last stage of washing.

Each stage comprises an agitator zone and a settling zone. A diagram of an agitator with the zones of retention by baffles is shown in Fig. 11; arrows indicate the paths followed by the soap and wash-lye.

The agitation takes place in a horizontal tube with an aperture through which the soap enters, while the lye is introduced by a pump from the settling zone of the superior stage into the axis of the agitator tube. The system is then vigorously agitated by paddles. The shaft of the agitator is mounted on Cardan joints.

The mixture flows from holes in the agitation tube and passes to settle. The hatched portion of Fig. 11 represents the mixing zone.

The soap passes easily through the different stages by gravity and by the impulse of the soap pump P3. On the other hand, contrary to what would be expected, experience shows that although soap washed with limit-lye settles

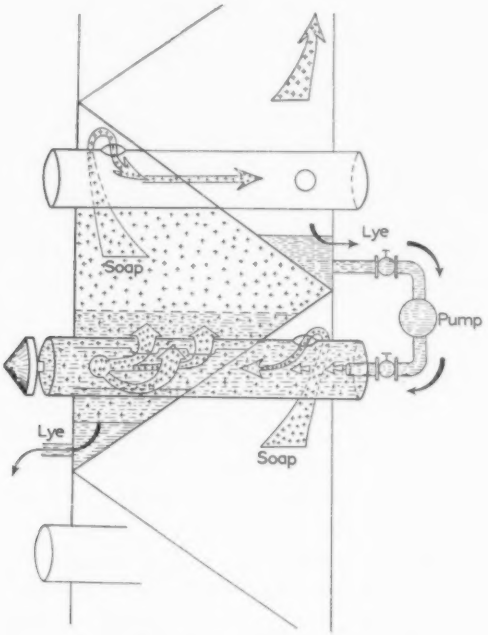

Fig. 11. Agitator.

rapidly, a simple tower with counter-current circulation of soap and lye will not suffice. The lye will not circulate by gravity in such a case. In fact, it was necessary to place pumps at each stage to propel the lye in a forced circuit.

The throughput is adjusted to slightly above the output actually required. This offers no inconvenience as a slight partial re-cycling of the soap is practically without effect on the yield.

Washing is carried out with the limit-lye previously determined in the laboratory. The first stage consists of a tube, leading into the agitator, through which the brine is injected by the salt-injection pump P4. The purpose of this low-pressure pump is to restore the system to the line EH, if the soap has not a comparison sufficiently close to H, by a small injection of saturated brine, as shown in Fig. 8. Introduction of a lye just stronger than limit-lye leads to a vicious circle since the crude soap must meet a lye which, having already been in contact with soap is at the lye limit or only very slightly below it.

In the last stage, there are introduced at the same time, in accurately measured quantities, the nigre or isotropic solution by the nigre pump P5, from the

settling batches, and being entirely re-cycled, and brine and water from the wash-pumps P6 and P7.

After agitation and separation, to introduce in the penultimate stage the subjacent lye, this must be rigorously controlled to the limit-lye concentration which will be maintained throughout the remainder of the operation.

It is therefore between the penultimate and final stages that the necessary adjustment is made. The lye is adjusted on the basis of a sample taken at this level (at point E in Fig. 9). The adjustment is simple, the limit-lye being known by laboratory determination and the influence of the nigre also being known. It can be made to within 1 per cent of the absolute value. Control of separation of the spent lye is also assured.

Six stages are necessary to obtain a satisfactory, say 94 per cent yield, in deglycerination. For more stringent demands the tower can function with any desired number of stages. An eight-stage plant is actually in production.

The spent lye is removed by the volumetric pump P8 from the settlement zone of the first stage.

The wash tower L has thick observation glasses at all stages.

C. Fitting

At the commencement of research on the process, it was proposed to wash the soap to eliminate impurities, to recover the glycerol, and also to avoid fitting. To that end, counter-current washing with brine at the limit-lye was carried out in the tower L which lead to a soap represented by point H on the ternary diagram and which contained a little lye of limit-lye concentration.

Such a soap was not commercially feasible and it had to be desalted. This was accomplished by washing with soda at a concentration electrolytically equivalent to salt at the limit-lye, which replaced a considerable part of the salt in the soap by alkali and which gave an alkaline soap.

The free alkali was therefore neutralized at first to the extent of 90–95 per cent with a suitable easily saponifiable fat such as coconut oil, and then with free fatty acids or a buffer such as acid sodium sulphoricinoleate.

At the end of this operation the neat soap is situated near G on the diagram (0·1–0·2 per cent NaOH).

The inconveniences of this first process, are principally those relating to adjustment. Inadequate adjustments lead to a final soap situated within the neat soap region and could have a viscosity varying from one sample to another. This could entail variations hindering the rate of formation of nuclei in the course of cooling, which could lead to difficulties in subsequent operations.

The measures of control were stringent and constant. They consisted of frequent photoelectric determinations of turbidity or alkalinity of water or alcohol solution of aliquots from the mass.

It has now been found preferable to introduce fitting. In this way there is gained a physicochemical equilibrium which avoids the necessity for a complicated and costly plant and there is the advantage of suppression of accidental fluctuations of composition and of production of a constant finished soap.

The object of fitting, as already mentioned, is to lead to a soap with a composition in the neighbourhood of H, but between G and H, which necessitates entering the region of separation, neat soap–isotropic solution. At a point H, the neat soap has maximum fluidity, a quality desirable in the subsequent treatments.

The washings which follow the fitting must be rapid and it is therefore necessary to obtain an isotropic solution as low in soap as possible. These conditions are best met by arriving close to point C, where the actual concentration of nigre is also that of C. A brine a little below the limit-lye permits an easy control of fitting. If it is neutral, however, the washing leads to an acid soap through hydrolysis. Consequently, in the Monsavon process, the soap is fitted directly with an alkaline lye (7 or 8 per cent NaOH for example). The soap and nigre obtained are alkaline. The re-cycled nigre maintains in the tower L an alkalinity sufficient to prevent the soap from becoming acid.

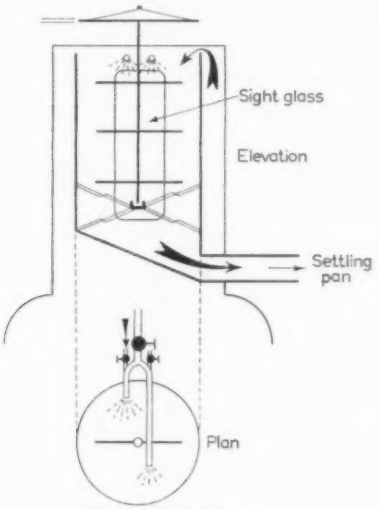

Fig. 12. Fitting box.

The fitting is carried out in the fitting box B, situated at the top of the washing tower L. The box has a hot-water jacket. Soap from the last washing stage enters the box, which is provided with a vertical agitator. The necessary quantities of water and caustic solution (supplemented in some installations with brine to avoid excessively alkaline spent lyes) are supplied by the adjustable fitting pumps P9 and P10.

The box B is furnished with a thick observation glass. It is shown diagrammatically in Fig. 12. The arrows indicate the direction of flow of the soap.

The neat soap–nigre system issuing from the box B passes to the settling pans (not shown in the layout in Fig. 9), where the soap and nigre separate. These two pans also have hot-water jackets, so that there also the settling can proceed at the equilibrium temperature indicated by the ternary diagram.

Alternate use of the pans permits continuous operation, one being filled whilst the other is being used for settling. Their capacity provides for 8–12 h settlement. For a plant delivering 2 tons of soap per hour, two pans with a capacity corresponding to 50 tons of soap are sufficient.

Settlement is, as usual, considerably influenced by the presence of gas occluded in the fat initially. It should be noted that in the case where a gas-free soap is obtained, settling is so rapid that a heated jacket is unnecessary and truly continuous settling is possible. In such conditions, for an apparatus giving 2 tons of soap per hour a pan with a capacity corresponding to 10 tons of soap will suffice (5 h settlement). As soon as one operation is finished, to change from one quality of soap to another, one can dispose of all the finished soap.

The level of nigre in the pans is generally kept constant since all the nigre is re-cycled. The temperature gradient in the fitting pans is 5°C, augmenting the region of the invariant.

The soap, once settled, is exactly the same as that which one would obtain in batches with the same charges. It is passed on for the customary operations of solidification, milling, addition of neutralizers, perfumes, superfatting, etc.

III. Balances and Controls

Balances and controls, which are interdependent, are governed by the properties of the systems envisaged, and by various economic considerations.

A. Controls and starting of the plant after stoppage

To establish the balance of an operation, particularly for the washing of soap, and hence for the control of this washing, one operates preferably as follows, it being understood that it is a question here of the different solutions concerned in this part of the process.

Consider the equation:

$$\text{Wash water} + \text{fitting water} = \text{spent lyes} - \text{salt injection}$$

which represents the state in the washing tower and in the settling pans.

The control of washing consists of keeping these waters constant in the plant. In case of doubt, a little more nigre than is formed is pumped in order to be sure that the level of it does not rise in the settling pan in course of filling.

For control of fitting, the procedure is as follows: A sample from the box B after fitting is centrifuged to find the proportions of soap and nigre. These being known, the quantity of electrolyte in the fitting lye is varied to give the required composition. Attention is called to the fact that the total quantity of this lye cannot be varied but only its alkali content, which cannot alter the rate of washing. The significance of this will be indicated later.

If there is too much nigre, the concentration is increased and conversely, always keeping below the limit-lye. It is necessary to enter the invariant region, and as high as possible, in order to obtain a good yield of soap of which the alkalinity is to be, for example, 0·10 per cent NaOH.

With a little practice these results are easily attainable. The control becomes easier with increasing concentration of electrolyte. Some installations provide

for the addition of brine to the alkaline fitting lye which permits less-alkaline spent lyes. The latter should not exceed 1·0 per cent NaOH. Moreover, the fitting lye should not contain less than 1·0 per cent, if one wishes to avoid hydrolysis of the soap.

The control of feeds of water, brine and nigre to the wash tower, is effected as already indicated by sampling from the lye-return line between the final and penultimate stages of the tower L.

Samples are also taken of the soap after fitting and the spent lyes. The laboratory examination indicates the nigre and the limit-lye.

The various volumetric pumps of the installation can be adjusted to deal with all the factors which influence the operation of the plant (composition of charge, concentration of soda and salt lyes, limit-lyes, etc.).

Consideration will now be given to the recommencement of the plant after a cessation, due, for example, to the factory working for only part of a day or, perhaps, after a weekend. At such a time, the homogenizer, reactor and soap vat are empty, but all the stages of the wash tower are full of soap and lye. This avoids the possibility of a soap blockage in the lye-return pumps, on re-starting.

Equilibrium temperature is first re-established and next, the fats and caustic lye pumps are started in order to deliver in the feed tanks for a certain length of time. These pumps then run and cause the valves to operate. The homogenizer is then put into action. The gap of the homogenizer is set for the predetermined emulsion and fat and soda are fed in by the saponification pumps. The emulsion flows into the reactor-tube. At the top of this tube there is a small vent which is left open temporarily until an efflux of emulsion shows that the reactor is completely filled. The pressure on the valve at the bottom of the reactor is then such that soap flows into the crude soap vat.

While this vat is filling, the pumps are adjusted and then soap, wash water and nigre are fed simultaneously to the wash tower. To ascertain if the concentration of lyes which have washed the soap are essentially that of limit-lye, a sample is taken from the lye circulating between the final and penultimate stages. If it is not so, it is rectified immediately.

The tower being full and the soap reaching the fitting box B, the fitting pumps are started and the installation is finally equilibrated.

B. Deglycerination yields—rate of washing

When the deglycerination yields of a soapery are considered, and more particularly in the case of the plant described here, it is less important to obtain the greatest yield possible, than to find the most economical working conditions.

The deglycerination yield depends on only two factors: the number of washes i.e. the number of stages in the tower L and the rate of washing, i.e. the ratio between the weights of alkaline salt-lye and soap in the neat phase introduced into the tower L.

It is obvious that, if for a given wash rate, one increases the number of stages in the tower, the yield of the apparatus and the concentration of the spent lyes are increased.

It is therefore necessary to find the most economical compromise. This can be arrived at by calculating the rate of washing as a function of the cost of evaporation for glycerol production per ton of water for the factory concerned. In this way a curve is obtained which represents the cost of concentration and by establishing also a curve for the yields of deglycerination in relation to the wash rates, one can find the economic yield.

Before giving, by way of example, a summary of the setting up of a balance for the whole operation, we shall first indicate the calculations for glycerol and salt.

C. Calculation of glycerol

This is based on the admission that at equilibrium between soap and lye, the glycerol is partitioned equally between the water in the soap and the water in the lye.

This being given, consider for example, the case of 100 kg of crude neat soap at 63 per cent fatty acids, a system corresponding to 69·5 per cent of soap and 0·5 per cent of various other substances. This system contains 30 per cent of water and glycerol.

Suppose that it contains 7 per cent of glycerol and is washed with 50 kg of lye. The total for the system is then 150 kg containing 80 kg of lye and glycerol.

On the above hypothesis, we have finally:

glycerol in the soap: $\frac{7 \times 30}{80} = 2{\cdot}62$ i.e., soap at 2·62 per cent glycerol

glycerol in the lye: $7 - 2{\cdot}62 = 4{\cdot}38$ i.e., lye at 8·76 per cent glycerol.

D. Calculation of salt

This is based on Wigner's rule, which says that the hydrate at 66 per cent fatty acids, which can be represented (Lachampt, 1955) by the point of intersection of the slopes which correspond to the equilibria between the neat soap on the one hand and the middle soap, isotropic solution and saline lye on the other hand, does not contain salt. That is, the point envisaged is situated on the axis of the ordinates in the ternary diagram in Fig. 8. This hydrate corresponds to 71·7 per cent of pure soap in the case of a charge of 3 parts tallow to 1 of copra; for the charge, 100 parts of fatty acids gives 108·65 parts of dry soap.

Consider then, 100 kg of soap at 63 per cent fatty acids and 0·2 per cent NaOH, which contains 68·5 kg of pure soap. The sodium hydroxide can be taken as electrolytically equivalent to 0·22 per cent NaCl.

Let this soap be washed with 100 kg brine at 9·2 per cent salt (a practicable limit-lye).

Initial state:

100 kg neat soap, i.e. 68·5 kg pure soap + 31·28 kg water + 0·22 kg salt.
100 kg lye, i.e. 90·8 kg water + 9·2 kg salt.
Total: 200 kg with 9·42 kg salt.

Final state (assuming complete settlement):

$$\frac{100 \times 68{\cdot}5}{71{\cdot}7} = 95{\cdot}5 \text{ kg soap at 66 per cent fatty acids without salt.}$$

$200 - 95{\cdot}5 = 104{\cdot}5$ kg salt water.
The soap at 63 per cent fatty acids finally contains:
$100 - 95{\cdot}5 = 4{\cdot}5$ kg salt water.
The respective percentages of salt are therefore:

$$\text{In the soap} = \frac{9{\cdot}42 \times 4{\cdot}5}{104{\cdot}5} = 0{\cdot}40 \text{ per cent}$$

$$\text{In the lye} = \frac{9{\cdot}42 \times 100}{104{\cdot}5} = 9{\cdot}01 \text{ per cent}$$

E. Specimen balance

Consider a charge composed of a mixture of 75 per cent neutral tallow and 25 per cent neutral copra. The tallow corresponds to 95·5 per cent fatty acids and 10·8 per cent glycerol whilst the copra corresponds to 94·4 per cent fatty acids and 13·7 per cent glycerol.

The mixture therefore contains:

$$\frac{(95{\cdot}5 \times 3) + 94{\cdot}4}{4} = 95{\cdot}2 \text{ per cent fatty acids}$$

and

$$\frac{(10{\cdot}8 \times 3) + 13{\cdot}7}{4} = 11{\cdot}5 \text{ per cent of glycerol.}$$

Moreover, 14·15 kg and 17·9 kg of pure NaOH are required respectively, for saponification of 100 kg each of tallow and copra. The weight of NaOH necessary to saponify 100 kg of mixture is therefore:

$$\frac{(14{\cdot}15 \times 3) + 17{\cdot}9}{4} = 15{\cdot}08 \text{ kg}$$

Allowing for approximately 2 per cent excess, 15·4 kg pure sodium hydroxide are required in all.

If one wishes to produce a soap at 63·4 per cent fatty acids, for example, a further calculation is necessary:

$$\frac{95{\cdot}2 \times 100}{63{\cdot}4} = 150 \text{ kg}$$

$150 - 100 = 50$ kg of caustic lye containing 15·4 kg NaOH

The concentration of this lye is therefore:

$$\frac{15{\cdot}4 \times 100}{50} = 30{\cdot}8 \text{ per cent NaOH}$$

Saponification in these conditions results in 150 kg crude soap containing 0·2 per cent NaOH which corresponds to 0·22 per cent of salt, a figure which must be known if the soap obtained is to be situated on the ternary diagram, and

$$\frac{11{\cdot}5 \times 100}{150} = 7{\cdot}66 \text{ per cent of glycerol}$$

For this substance a certain reduction corresponding to unsaponifiable matter is allowed and 7·35 per cent is ultimately taken as the figure for glycerol.

There are now 100 kg of soap at 63·4 per cent fatty acids. To this soap which is about to enter the wash tower, there must be added (by pump P4) a certain quantity of salt such that the soap will be brought to a fatty acid content equal to that which it would normally have at equilibrium in the tower, say 57 per cent.

By application of Wigner's rule, one can calculate readily, the quantity of water to the limit-lye that such a soap contains when in equilibrium with this lye:

$$100 - \frac{57 \times 100}{66} = 13{\cdot}64 \text{ kg of water to the limit-lye}$$

If this limit-lye is at 9·2 per cent NaCl, for example, the weight of sodium chloride in the soap at 57 per cent fatty acids is then 1·227 kg. As the soap already contains free alkali electrolytically equivalent to 0·22 per cent NaCl, the quantity of salt to be added is, in fact 1·007 kg which, as 26 per cent saturated NaCl brine, is 3·87 kg that is to say about 4 kg of saturated salt solution per 100 kg of soap.

Finally, suppose that it is desired to obtain a 95 per cent glycerol yield, and that the rate of washing for this yield is 0·65. It is necessary first to have, after washing and fitting, 100 kg of soap at 63·4 per cent fatty acids and 65 kg of spent lye.

In these conditions, there are

$$\frac{7{\cdot}35 \times 95}{100} = 6{\cdot}98 \text{ kg glycerol in the spent lye of which the composition is:}$$

$$\frac{6{\cdot}98 \times 100}{65} = 10{\cdot}7 \text{ per cent glycerol,}$$

while the soap finally contains:

$$7{\cdot}35 - 6{\cdot}98 = 0{\cdot}37 \text{ per cent glycerol.}$$

IV. Advantages and General Considerations

A. Space required and recirculation of the nigre

A good recovery of glycerol in batches demands a considerable capacity to carry out the correct counter-current washing and also considerable storage capacity for lyes.

Moreover, a washing in batches which gives an acceptable glycerol recovery does not sufficiently refine the soap and if the nigres are re-cycled in an identical charge, the quality of the soap is lowered.

Toilet soap factories are thus obliged to have a second quality of soap to provide an outlet for the nigres or are obliged to recover the fatty acids from the nigres and distill and re-introduce them into the circuit, with all the inconvenience that this entails.

In the Monsavon process, on the other hand, the size of the plant is greatly reduced and the nigre is totally re-cycled with the exception of the impurities which all pass into the spent lyes.

B. Control

Since everything is measured, the balance of the process can be found instantaneously. The input, output and stocks at any given time are known accurately.

This point, although it may appear less important than others, may be, however, a valuable consideration as it avoids waste. In a factory working with batches, a glycerol balance is practically impossible, because of numerous serious losses which cannot be detected in time, and poor results must often be tolerated. Only one workman is needed to operate an installation. Stopping and restarting do not require additional labour.

C. Flexibility

Everything is jacketed and insulated. Stopping and re-starting can be effected without emptying the whole plant. Production can therefore be continuous or on a 12 h basis, and even to stop at the weekend for 2 or 3 days, the plant need not be emptied. For a stoppage of 3 days it is not even necessary to keep hot water circulating: one merely recommences heating a few hours before re-starting. The only precaution required is to stop the circulating pumps between the stages 5 min before the general shut-down in order to have lye in each of these stages so that the pumps have lye to transfer from stage to stage on re-starting.

D. Power consumption

The requirements are some 80 kg of steam per ton of soap manufactured, and 25 kW for a plant delivering 2 tons/h.

E. Charging

All types of charge can be used, entailing the most diverse limit-lyes, from, for instance, pure sulphur oil soap at 4 to pure coconut oil soap at 23.

Fats high in unsaponifiable matter, such as shea butter, can be used without inconvenience. The diene hydrocarbons do not have time to polymerize during saponification. Although not eliminated, they are so finely dispersed in the finished soap that they do not cause subsequent rancidity.

F. Purity of soap

In all cases, the soap is at least as good as that prepared by any other process. In many cases, with certain raw materials, it is distinctly better. It is particularly suitable for the production of toilet soap, for the peroxides are eliminated in the waters, and scleroproteins are not subjected to the degradation which occurs with prolonged boiling with caustic. The soap does not have the characteristic household washing smell so difficult to cover with perfume.

The spent lyes, containing the oxyacids, phospholipids and non-degraded scleroproteins and other trace materials are easy to treat. Clarifications are good even with oxidized fats.

G. Disadvantages

Some drawbacks can be noted. First of all, the cost of the process is relatively high and consequently rational factory organization must exist for its application. There are unfortunately many empirically operated soaperies, and although the robustness of the plant permits rough treatment, it cannot be used everywhere.

Since saponification is complete before washing and the wash waters have to be alkaline to prevent hydrolysis, the spent lyes are therefore more alkaline than those from batches.

When the plant is efficiently operated there is from 0·4 to 1·0 per cent of NaOH in these lyes. This difficulty is easily overcome by neutralizing the spent lyes with the charge, which is always acid.

Also, it is necessary to have homogeneous charges. Although that is always easy, the preparation of the charges can sometimes be laborious, especially in the case of complex charges based, for example, on various soapstocks, resins and miscellaneous fatty materials,

Thus it is found preferable in many cases to use the process without the continuous saponification, this being then performed in batches, simply by boiling for 3 h and then applying the rest of the process as previously described.

This variation is used frequently, as mentioned, for complex charges and also where batches are available as, for instance, in the case of modernization of existing factories, and although less elegant, also gives excellent results.

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3

PROGRESS IN THE TECHNOLOGY OF SOYBEANS*

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* In this chapter, the author has attempted to cover progress in soybeans from 1949–1954. Selection was based on present and possible future importance of the items chosen.

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PROGRESS IN THE TECHNOLOGY OF SOYBEANS

J. C. Cowan

I. Introduction

During the past 20 years the United States has become the leading producer of soybeans in the world. Its production has increased from 14 million bushels in 1930 to over 300 million bushels in the 1950s. This growth has come in three distinct stages. The first stage was a gradual growth in the 1930s until a production of 90 million bushels was obtained in 1939. World War II brought about the second big growth in soybean production with the annual production increasing to 192 million bushels in 1944 and 1945. In 1950, soybean production took another jump to approximately 300 million bushels and continued at that rate in 1951 and 1952.

Although dry weather reduced yields in 1953 to about 260 million bushels, more favourable but not ideal weather permitted a production of over 340 and 370 million bushels in 1954 and 1955. The last jumps in soybean production made the United States a bigger producer than China, and thus the leading producer in the world. A summary of world soybean production in specified countries is given in Table 1 (World Soybean Production, 1955, 1956)

In the Far East soybeans are produced primarily for human food. There they serve as a basic food material for the production of soy sauce, monosodium glutamate, vegetable milk, tofu or soybean curd, yuba, miso, and a variety of other fermented products. In the United States, soybeans have been grown primarily for oil, and the resulting meal is used as a feed for livestock and poultry. Success can be attributed to the following: (a) the development of improved varieties and adaptation of the varieties to mechanical rather than hand harvesting, (b) technological improvements in the production and processing of soybean oil for use in food products, and (c) proper processing of the residue from oil extraction to give a highly nutritious meal which is one of the best sources of protein for livestock and poultry feeds. Thus, most American farmers have the choice of soybean as a second cash crop in addition to corn, wheat or cotton.

II. Soybean Production

In the 1920s varietal improvement led to a shift in soybean production in the United States from the south-eastern states to the middle west. A host of new varieties was created by the agronomists to meet the varied soil and climatic

*Table 1. World soybean production**

Country	*Acreage* (1,000 acres)				*Yield* (bushels/acre)				*Production* (1,000 bushels)			
	Average 1945–49	1953	1954†	1955†	*Average* 1945–49	1953	1954	1955†	*Average* 1945–49	1953	1954†	1955†
Canada	73	216	254	214	20·5	20·4	19·5	26·0	1,491	4,406	4,953	5,650
United States	10,649	14,679	16,971	18,559	19·6	18·3	20·1	20·0	208,885	268,528	341,565	371,276
China (Est.)	11,256	—	—	—	16·9	—	—	—	190,248	198,000	320,000	330,000
Manchuria (Est.)	7,048	8,200	—	—	16·5	16·3	—	—	116,475	134,000	‡	‡
Indonesia	872	1,161	—	—	11·2	9·3	—	—	9,736	10,839	14,567	15,000
Japan	612	1,041	1,082	1,054	12·1	15·1	12·8	18·0	7,432	15,777	13,816	19,000
Korea (South)	583	617	637	—	8·5	8·1	8·8	—	4,984	4,995	5,628	18,200
Brazil	23	148	170	170	19·0	21·9	25·0	21·6	446	3,242	4,042	3,674
World total (Est.)	32,675	39,660	42,700	44,220	—	—	—	—	551,540	651,250	716,125	760,535

* Years shown refer to years of harvest. Southern hemisphere crops which are harvested in the early part of the year are combined with those of the northern hemisphere harvested the latter part of the same year.
† Preliminary.
‡ Included in China.

conditions. This varietal improvement is shown in the increase in the average yield per acre from 11 bushels in 1924 to 18·7 in 1937–41, 19·4 bushels in 1946–48, and 21·4 bushels per acre in 1949–52. The average yield in the states of the soybean belt runs somewhat higher than this, with Illinois usually reporting 24–25·5 bushels per acre each year. Many farmers in this area average 30–40 bushels per acre, with individual reported yields running as high as 63·6. Yields as high as 100 bushels per acre have been reported from Japan, and the Canadian record is 67·9 bushels per acre (RECORD YIELD 1955, 1956)

New developments in soybean production which may become important in the future are the increased production in the southern United States and production in Brazil. The Brazilian activity has occurred in Rio Grande do Sul and Sao Paulo where approximately 2½ million bushels of soybeans were produced in 1951 and 1952, and over 4 million in 1954. In the southern United States, production increased almost six-fold between 1945 and 1955, from 10 million to 59 million bushels, with Arkansas production 21 million bushels. Soybeans have also spread north, with Minnesota's production rising almost seven-fold from 6·7 million to 45 million bushels in this same period.

Agronomic research has been a major factor in the earlier as well as the recent increased production. This research is co-ordinated by the U.S. Regional Soybean Laboratory and the U.S. Department of Agriculture, by co-operating with the State Agricultural Experiment Stations in the various states. This programme has made it possible to develop new varieties more suitable for the particular growing areas involved. Undoubtedly new varieties will be developed with increased yield per acre and improved growth characteristics. Though the midwestern states may continue to be the major producers of soybeans, the southern states may become a factor in the over-all production and utilization of soybeans in the United States. Fig. 1 shows the various localities where the different varieties are recommended for growing (AGRONOMISTS OF SOYBEAN GROWING STATES, 1956).

Another major factor in the soybean industry in the United States is the increasing importance of diseases. As yet these diseases have not caused any widespread or serious damage. But it is expected they will become more serious as more and more soybeans are grown. They are particularly important where soybeans are grown on the same land for several years. The more important diseases are stem canker, bacterial blight, bacterial pestule brownspot, pod and stem blight, brown stem rot, mildew, mosaics, frogeye, and root rot. Strains resistant to bacterial blight, brownspot, and frogeye have been found, but strains resistant to the more destructive diseases in the North Central area, stem canker and brown stem rot, are still to be located (WEISS, 1953).

Soybeans are one major farm crop which benefit from the presence of proper flora or bacteria in the ground where they are grown. Normally, it is recommended that a field not previously used for producing soybeans should be inoculated with the proper type or types of bacteria, such as *Bacillus radicocla*. If soybeans are not frequently grown on this land thereafter, inoculation should be practised with each planting. Varieties appear to differ in the strain of bacteria

which is most effective in increasing yields. This relation between the soybean plant and nitrogen-fixing bacteria is known as a synergism. No added nitrogen fertilizer is necessary for soybeans if the field is well inoculated with these bacteria. Indeed, soybeans grown for beans can be used to increase nitrogen content of the soil (SEARS, 1939).

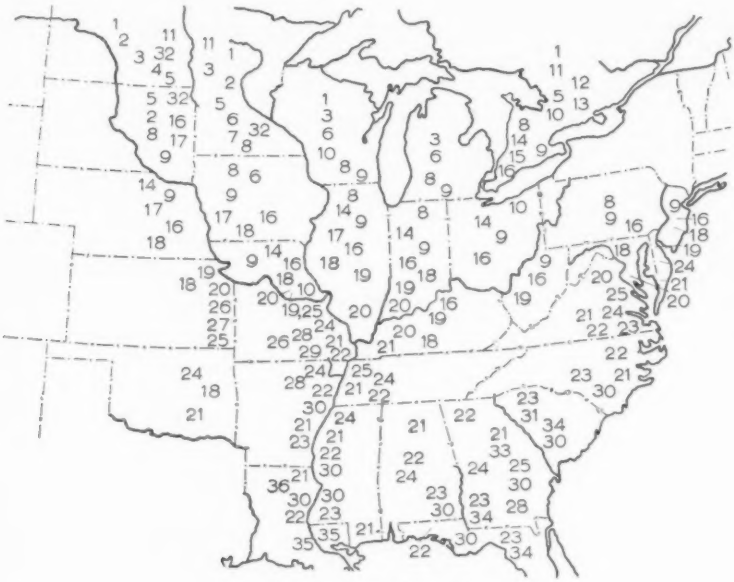

Fig. 1. Best adapted varieties.

Key to Fig. 1.
1. Flambeau; 2. Ottawa Mandarin; 3. Norchief; 4. Goldsoy; 5. Capital; 6. Chippewa; 7. Renville; 8. Blackhawk; 9. Hawkeye; 10. Monroe; 11. Acme; 12. Comet; 13. Hardome; 14. Harosoy; 15. Harman; 16. Lincoln; 17. Adams; 18. Clark; 19. Wabash; 20. Perry 21. Ogden; 22. Lee; 23. Jackson 24. Dorman; 25. S—100; 26. Chieg; 27. Hong Kong; 28. Dortchsoy 67; 29. Dortchsoy 2; 30. Roanoke; 31. C.N.S. 4; 32. Grant; 33. C.N.S.; 34. J.E.W. 45; 35. Improved Pelican; 36. Volstate.

The most desirable time for planting soybeans varies considerably, depending on the latitude, variety, and weed competition. In the north central area of the United States, adapted varieties planted between May 10 and 25 give highest yields. In the midsouth, plantings before May 1 make only stunted growth and stimulate weed competition, while along the Gulf Coast the short day stunts growth if soybeans are seeded before May 15. Planting should be completed by June 15, but later planting can be practised when sufficiently early varieties are used. Some reports indicate that very early varieties of soybeans have been grown with moderate success after the harvesting of a winter grain crop (WEISS, 1953).

Latitude also determines the row width for maximum growth, with 18 in. rows giving maximum yields in the northern part of the growing area. In the major producing north central area, 21–24 in. give optimum yields, while 40 in. rows give optimum yields with adapted varieties in the south (PELLET, 1953).

Weed control is a very important factor in soybean production. Recent work showed that weeds, such as foxtail and smartweed, can reduce yields as much as 10 per cent. Reduction in yields occurred when early but not immediate removal of weeds was practised. Row planting is the preferred practice for soybeans primarily because weeds can be controlled properly through cultivation. Recently, herbicides have been recommended for use as pre-emergence sprays. Six to eight pounds per acre of dinitro [dinitro-*o*-(sec. butyl) phenol] and '3 chloro-IPC' [*iso*propyl-*N*-(3-chlorophenyl) carbamate] have been used to control early weeds with 0–95 per cent effectiveness. When soybeans are 4–8 in. high, 2,4-dichloro-phenoxyacetic acid at the rate of 1 oz per acre has been successfully used as an emergency measure. At harvest time, defoliants can be used to kill weeds when weeds are serious enough to delay harvesting until after the frost kills the weeds but reduction in yield can result if defoliant is used before maturity is reached (Silfe, 1953)

Soybeans will respond to application of nitrogen fertilizer only if the field does not have a sufficient supply of synergistic bacteria. However, application of other types of fertilizer can increase yield if the soil is deficient in minerals, such as potassium, calcium and phosphorus. Soybeans contain substantial amounts of minerals and they deplete the soil of minerals. Studies have shown that when soybeans are grown for beans and the straw is returned to the soil, the practice can add 16 lb of nitrogen and remove 8 lb of phosphorus, 25 lb of potassium, 2·8 lb of calcium, and 3 lb of magnesium per acre in one crop year.

Another major loss in production of soybeans occurs when the beans are harvested. Field loss is estimated at 10–25 per cent and an 8 per cent loss is considered reasonable. As varieties become taller and beans farther from the ground, and with improvement in combining equipment, field losses should be reduced.

III. Storage and Handling of Soybeans

With the increasing production of soybeans during the past 15 years, the marketing of soybeans has not been an orderly procedure. Until recently, most of the soybeans came to market during an 8-week period immediately following the harvest. Appearance of over 100 million bushels on the market during this period naturally had a somewhat depressing effect on the price received.

Holman and Carter (1952) have reported soybeans with 10 per cent moisture or less remained in generally good condition up to 4 years, although some decrease in germination occurred after the first year. At about 12 per cent moisture, market grades held up for nearly 3 years, but germination and other values declined gradually. At 13 per cent moisture, safe storage was limited to one winter season from harvest to late spring. At 14 per cent the safe period was limited to the winter months. Soybeans with moistures of 15 per cent or more usually should not be stored in farm-type bins. If beans from the field have too much moisture in them, it is best to condition them by drying with forced heated or unheated air when air temperatures are above 60°F and the relative humidity is below 75 per cent. In order to store a good grade of dry beans properly, it is necessary to have weather-tight bins in order to prevent damage caused by

leakage (HOLMAN and CARTER, 1952). As the moisture content of the beans drops below 9 per cent increasing difficulty is encountered in handling with modern equipment. Splits, loss of seed coat, and other damage occurs. Lower germination is also associated with beans which are too dry at harvest.

Normally, soybeans flow from the farmer to country elevators by truck, and to terminal elevators and processing plants by rail, truck, and barge. Most of the processors operate large elevators with a storage capacity often as high as 7 million bushels. These elevators are usually reinforced concrete structures consisting of large circular bins with intersticed bins, a work house, and sometimes separate drying and dust houses. The circular bins or silos are 20–40 ft in diameter and stand 150 ft or more high. They are arranged to make maximum use of the space between them. Railway cars or trucks are unloaded by power shovels which push the beans out of the car, or by car unloaders which tilt the railway car or truck to drop the soybeans into the hopper. The beans are conveyed and elevated to hopper-bottom bins located directly over the scale hoppers. A spouting assembly located just below the scale hoppers directs the beans to conveyors and elevators which deliver the beans to storage, processing, driers or cleaners. Some of the storage bins have temperature-measuring equipment such as thermocouples, which measures accurately the temperature of the beans at intervals of 6 ft from top to bottom of the bin. With a centralized system it is possible to check accurately the temperatures in the bin. Rapid increase in temperature (hot spot) recorded by any thermocouple usually results in these beans being processed immediately or their being turned over and moved to other storage bins. Such hot spots usually result from high moisture content.

IV. GRADING

Soybean grades were established by an Act of Congress known as the United States Grain Standards Act administered by the U.S. Department of Agriculture. Soybeans were classified as a cereal grain. Regulations were published in the *Handbook of Official Grain Standards of the United States* which was issued by the PRODUCTION and MARKETING ADMINISTRATION in 1949. The soybean grades, taken from the handbook, are shown in Table 2, and the changes adopted in 1955 are indicated.

Before the 1953 crop, No. 2 Yellow Soybeans were usually the highest grade seen in normal trading. In 1953, a considerable quantity of beans were sold as No. 1 Yellow Soybeans. Moisture content of 1953 beans was very low, the quality of a portion of the production was very high, and stiff competition for beans, particularly for export, may have been responsible for this change in trading practices. Reports indicate that shipments of beans to Europe have been plagued in recent years by high amounts of foreign material, primarily weedseeds. Illegal practices in grain handling and the high permissible amounts of foreign material in No. 2 beans as compared with the lower permissible amounts in high grades of other grains appear to have fostered shipping of lower quality of soybeans to market and to Europe in recent years. Vigorous action by the American Soybean Association to determine the reasons for European

Table 2. Soybean grades

Grade	*Minimum test weight per bushel* (lb)	*Maximum limits of*				
		Moisture (%)	*Splits* (%)	*Damaged kernels (soybeans) and other grains* (%)	*Foreign material*	
					Old (%)	*New* (%)
No. 1*	56	13·0	10	2·0	2·0	1·0
No. 2*	54	14·0	20	3·0	3·0	2·0
No. 3*	52	16·0	30	5·0	4·0	3·0
No. 4†	49	18·0	40	8·0	6·0	5·0
Sample grade	Sample grade shall be soybeans which do not meet the requirements for any of the grades from No. 1 to No. 4, inclusive; or which are musty or sour, or heating; or which have any commercially objectionable foreign odour; or which contain stones; or which are otherwise of distinctly low quality.					

* The soybeans in grade No. 1 of the class Yellow Soybeans may contain not more than 1·0%, in grade No. 2 not more than 2·0%, and in grade No. 3 not more than 5·0% of Green, Black, Brown, or bicoloured soybeans, either singly or in combination.

† Soybeans which are materially weathered shall not be graded higher than No. 4.

‡ Special limits on heat damage, redefining of splits as pieces of soybeans, and restriction of purple mottled or stained soybeans to not higher than No. 3 were other changes.

reluctance to purchase beans under U.S. Standards and the prosecution and conviction of persons responsible for illegal handling of grains for foreign shipment, have done much to improve the quality of foreign shipments from the United States.

Oil content of the beans was used during World War II as the basis in trading, but it has not been used generally since 1945. Beans from certain areas where oil content is low have been avoided by processors. Inasmuch as oil is a major product from soybeans, it appears that grading based on oil content should have a more firm basis (Hilbert, 1946).

Early in 1955, hearings were held to determine whether the grading of soybeans should be changed and the changes listed as 'new' in Table 2 were established (Changes in U.S. Standards, 1955). These changes should improve quality of beans available for foreign trade as well as for domestic processing. In addition, segration of beans from Illinois, Minnesota, and from all other points has been initiated at one large port which supplies much of the foreign market.

V. Removal of Oil from the Soybean

United States processors have used two traditional major methods for removing oil from the beans: continuous screw pressing and solvent extraction. Pressing was introduced early in the history of soybean processing in the United States and was the principal method of processing during the early development of the industry. Hexane extraction was introduced in the 1930s. As soybean production climbed rapidly in the early 1940s, screw pressing in the industry accounted for 70 or more per cent of total oil production. However, when the production of

soybeans took a second major jump in 1950, the swing to solvent extraction with petroleum hydrocarbon gained momentum and is now dominant. In 1951–52, 74 per cent of the soybeans processed were extracted to obtain the oil. In 1952–53, the trend continued despite a big crop of soybeans, because large processors continued to add capacity for solvent extraction and to retire screw presses. In 1953–54, the shortage of beans and a price relationship between beans, oil and meal which did not permit profitable operation for certain periods probably reduced the total quantity of beans processed, but particularly those processed by screw pressing. Consequently, in this progress report on the technology of soybeans only solvent extraction will be discussed.

A. Preparation of flakes

In most solvent extraction plants for soybeans, the flaking operation is considered exceedingly important. First, it is customary to remove tacks, nails, and other ferrous materials by passing the soybeans through a magnetic separator. The cleaned beans are cracked by passing them through rolls which have cutting corrugations threaded around the roll and feeding corrugations running the length of the roll. Cracking rolls are usually arranged in pairs stacked two or three high. In some plants, scourer–aspirators, such as Entoleters, are used to effect a preliminary dehulling after passage through the cracking rolls.

Most mills now have dehulling equipment, which may consist of an air suction on the top of a solid stream of cracked beans, a centrifugal separation, or a screen followed by aspiration. The cracked beans are conditioned usually to about 10–11 per cent moisture, heated to 145–160°F, and while still hot passed through the flaking rolls, which are usually 20–24 in. in diameter and 40–44 in. wide. Conditioning of cracked beans just prior to flaking is practised to reduce fines and give a stronger flake. Proper feeding from a corrugated roll to the flaking roll is necessary to achieve proper distribution of flakes and to obtain the proper thickness of flakes.

Tests conducted by the percolation method with flakes from different varieties and production years showed a remarkable uniformity in the time required for extraction to 1 per cent residual oil. This relation can be expressed as:

$$\log T = n \log D + \log K$$

where T is time in minutes to 1 per cent residual oil on a dry basis, D is the effective extraction size or thickness in inches, n is the slope of the line and K equals the intercept at 1·0 in. ordinate. The value of n for soybean flakes is 2·5. The crucial thickness for flakes in most soybean plants is about 0·01 in. If this thickness increases to 0·015 in. the time required to extract to 1 per cent oil at the boiling point of the hexane or 150°F is increased from 6 to 29 min. At a comparable flake thickness, a reduction in temperature of extraction from 150 to 95°F increases the time for extraction from 13 to 32 min (National Soybean Processors Association, 1954–55). For economic reasons the flakes must not remain in the actual extraction unit any longer than necessary; strict co-ordination of the flake thickness, time for extraction and temperature of extraction

must therefore be maintained. Most plants check on the efficiency of their operation by determining oil content of the extracted flakes.

B. Solvents

The choice of solvents for extraction of soybeans is somewhat limited because the solvent should be readily available, be comparatively low boiling with a low heat of vaporization so that it can be readily and cheaply removed from the oil and the flakes, be comparatively non-toxic, have a high solubility for oil to permit reasonable solvent to flake ratios, and be non-inflammable, non-corrosive and inexpensive. No solvent meets all these requirements. The preferred solvent at the present time is in the petroleum hydrocarbon fraction, called commercial hexane, that boils in the range 146–157°F. Some plants are reported to be using heptane–hexane mixtures that boil in the range 157–207°F. Other solvents which have received some commercial attention are trichloroethylene and ethyl alcohol, especially the former. Despite outbreaks in 1912 in England, and in 1923–25 in Germany and the low countries, of a haemorrhagic aplastic anaemia in cattle resulting from feeding soybean oil meal extracted with trichloroethylene, commercial use of the solvent increased between 1942 and 1951 because apparently non-toxic meals were produced and used. However, outbreaks of this toxicity did occur after 1948 throughout much of the area immediately surrounding the plants using this solvent and in many places throughout the world where the meal was shipped. Toxicity of the trichloroethylene-extracted soybean oil meals varied considerably. In tests, some meals fed at low levels gave good growth and no signs of toxicity in 90 days, but other meals fed at the same level gave typical symptoms within 30–40 days. The use of this solvent for extracting soybeans for production of meal for livestock feeds therefore cannot be recommended.

Ethyl alcohol was used in a 100 ton per day plant at Darien, Manchuria and by the South Manchurian Railway for a number of years prior to the collapse of the Japanese forces at the close of World War II. Studies in the United States have considerably extended our knowledge of extraction with alcohol (Beckel *et al.*, 1948 a, b; Harris and Hayward, 1950), and commercial extraction was seriously considered by one major processor. This recent work showed that soybean flakes can be dried to about 3 per cent moisture and extracted with ethanol or *iso*propanol at a 4 : 1 or 6 : 1 ratio of solvent to flakes. Upon cooling, the resulting miscella gives three layers, consisting of an alcohol layer containing sugars, carbohydrates and other materials in solution; an interface layer; and an oil layer containing a small amount of alcohol. This separation of oil from a major part of the solvent without distillation permits some saving in operations over previous alcoholic processing methods. The oil produced in laboratory studies was essentially non-break except for darkening on heating, and the resulting meal was light coloured and almost bland to the taste. A schematic diagram of the proposed process (Beckel *et al.*, 1948b) is shown in Fig. 2.

The colour, acid number, and percentage break of oil samples prepared in the

laboratory with ethanol, trichloroethylene and hexane are shown in Table 3. The meal and acid-precipitated protein derived from alcohol-extracted meal were also light coloured and superior in colour and taste to that from hexane extraction. However, the fluctuating price of ethanol, the high solvent to flake ratios required, the legal restrictions involved in the use of ethanol, the failure of *iso*propanol to give products equal to those obtained with ethanol, and improvements in hexane processing are factors that have deterred the use of alcohols. Although it is agreed that alcohols would be somewhat less hazardous than

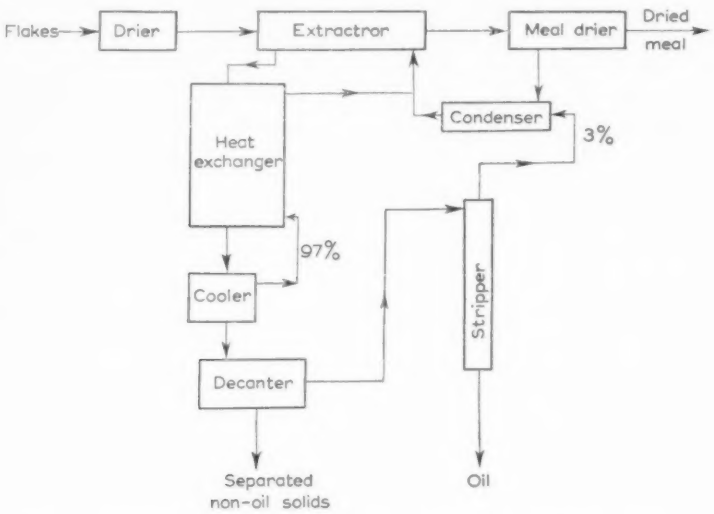

Fig. 2. Schematic diagram for the extraction of soybeans with ethyl alcohol.

commercial hexane, both are hazardous to use. In some countries where the price of alcohol is low in comparison with hexane, and where a need exists for improving the flavour of the extracted flakes for use in foods, alcohol may become the preferred solvent. Although there is a definite interest in a suitable non-inflammable solvent for extracting soybeans, none is so far available.

Table 3. *Characteristics of soybean oil extracted by different solvents*

Solvent	*Lovibond colour*		*Acid no.* (%)	*Break* (%)
	Yellow	*Red*		
Trichloroethylene	70	10·3	1·04	1·00
*iso*Propanol	70	12·8	0·95	0·86
Ethanol	70	2·9	0·06	0·00 darkens
Hexane	70	7·0	0·50	0·50

C. Extraction equipment and processing

Some of the basic ideas now used in much of the equipment for the extraction of soybeans were developed initially in Germany. One development was the basket-type extractor wherein the baskets are attached to an endless chain (the Hansa–Mühle or Bollmann extractor), and another was the vertical U-tube type extractor (Hildebrandt extractor). The Bonotta extractor was developed in the United States, and modifications of it are sold by both the Allis–Chalmers Manufacturing Company and the V. D. Anderson Company. This is a vertical gravity extractor of the immersion type. Various modifications have been described in considerable detail in scientific periodicals and books and no further description will be given here.

New horizontal extractors are being used to some extent on soybeans. Until recently the Kennedy and full-immersion screw-driven extractors were the only horizontal types being used. Although the advantage of gravity flow is lost, better control and redistribution of the miscella in successive flows through the meal are achieved. A preliminary soaking operation such as that included in the filtration–extraction processing, in the Rotocel extractor, and new horizontal basket-type extractors is advantageous to soybean operations. The progressive stepwise counter-current flow of solvent and meal permits withdrawal of miscella or admission of new solvent at any desired point. Thus, flexibility is achieved both in operation and in type of oilseed which can be processed. However, these operations are not described here since the principles involved are not radically new and they have been, in part, described in recent books.

D. Filtration–extraction

In 1954, the first filtration–extraction plant for the extraction of oilseeds went into commercial operation at Greenwood, Mississippi. Although this system was developed primarily for cottonseed, it is applicable to other raw materials, including soybeans (D'Aquin, *et al.*, 1954). Salient features of this system are: pre-cooking the flaked oilseed, soaking with solvent, separation of solvent from flakes by filtration in a continuous horizontal vacuum filter, and desolventizing of the oil and meal. The filter is the unique part of this system.

A diagram showing the flow of various streams for the process is illustrated in Fig. 3. Soaking of the flakes is effected in the slurry mixer–conveyor, and the first filtrate from drain No. 1 is pumped back and sprayed on the filter cake just after it is formed. This re-cycling of the miscella from the soaking operation reduced the fines content very substantially in cottonseed operations and would be a useful improvement in soybean processing. A 24 in. × 110 in. plain Dutch weave wire filter cloth was recommended filter. The filtrate from the second drain goes to the oil recovery system, whereas the filtrate from the third drain goes to the soaking operation. Filtrates from drains 4 and 5 wash the flakes prior to becoming filtrates from drains 3 and 4, respectively.

Residual lipid in the extracted meal from cooked flakes varied from 0·57 to 1·21 per cent and averaged 1·01 per cent. Raw flakes required a higher solvent

to flake ratio than cooked flakes. The main advantage of this extraction appears to be the flexibility in type of raw materials which can be processed. Thus, small and medium-sized mills might find this type of extraction very helpful where a variety of materials are available (D'Aquin *et al.*, 1954).

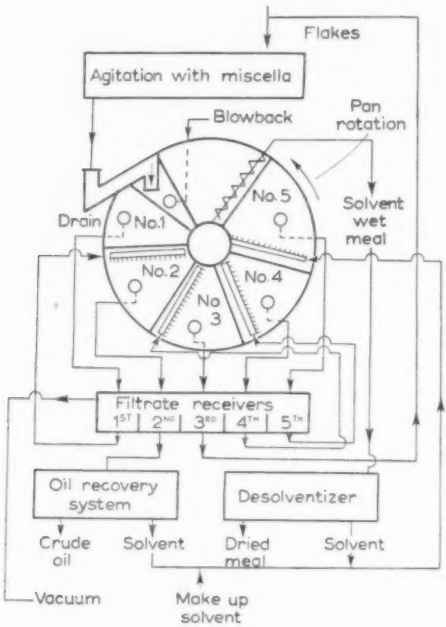

Fig. 3. Schematic diagram showing operating parts of the process for filtration–extraction.

E. Pre-pressing of soybeans

Another method of oil removal is a combination of pressing and extraction. Most vegetable fatty raw materials need some treatment to avoid the formation of fines—particles of the seed carried along with the miscella. Fines will clog filters, will not settle readily, and will slow or even stop production.

Fines are generally only a minor problem with raw soybean, but a major problem with raw flaxseed, cottonseed, and oilseeds of high oil content, requiring extraction of the untreated flakes or ground material by mechanically difficult operations which are economically unsound. However, proper treatment of the raw materials will give a better flake or cake for extraction. A primary treatment in most of these methods is heating. In pre-pressing, all materials are usually precooked, and then pressed in continuous screw presses to a comparatively low oil content. Studies made by Dunning and Terstage (1954) showed that pre-pressing could be used as a step in processing of soybeans. The oil could be reduced readily to less than 10 per cent in the pre-pressing. However, the resulting cake could not be extracted at a higher rate than standard soybean flakes.

VI. Removal of Solvent from Flakes

A. Desolventizer–toaster

One of the more important developments of the last 5 years in soybean technology is a new procedure for removing solvent from the flakes and for toasting. The desolventizer–toaster described by Kruse (1952) combines these two operations in a single steam-jacketed tower similar in design to the toasters or cookers commonly employed in the soybean industry. This cooker consists of a series of steam jacketed compartments with centre shaft fitted with blades for sweeping the flakes around the compartment to a port through which the flakes drop to the next compartment. Large amounts of steam are preferred in the top compartment to remove solvent which is vaporized to a condensing tube. The heat transfer from steam to solvent condenses the steam, vaporizes the solvent, and at the same time permits the flakes to absorb water evenly. The top compartment actually replaces both the desolventizing equipment and deodorizing tubes ordinarily used for removing solvent, and the flake mixers that raise the moisture content prior to cooking the meal. The desirable moisture content of the flakes entering the second compartment is about 15 per cent but it can run as high as 25–30 per cent or higher. The desirable top temperature is probably around 230°F, but satisfactory operation can be obtained at temperatures of 225–265°F.

A specific example may be described as follows. Soybean flakes which are still wet with hexane solvent are continuously fed at the rate of 28 ton/h into a vapour-tight, steam-jacketed cooker mentioned above (Fig. 4). Direct steam at the rate of 2 ton/h is introduced into the top compartment. Sufficient solvent (usually 35 lb) must adhere to the flakes entering this top compartment to condense enough steam to raise the moisture content to 15 per cent. The quantity of steam needed may amount to over 1,200 lb, depending on the moisture content of the flakes entering the desolventizer, usually about 8 per cent of the total weight. The presence of the solvent is also important because lack of it may lead to unequal application of moisture and formation of glue-like masses. The solvent is vaporized and the temperature of the flakes rises very rapidly to 210°F. Jacket heating with steam, the continual movement of the flakes and the direct application of steam to the flakes in the first compartment give violent agitation, and the moisture is then distributed throughout the flakes. The temperature rises as the flakes pass down through four to six more compartments. When a temperature of 220°F is reached, the evaporation rate of the water in the flakes equals the condensation rate. In the last compartments drying occurs and the temperature of the flakes increases to 230°F; moisture content of the final flakes is 13–15 per cent. Further processing of the flakes to meal lowers the moisture content to the accepted level of 12·5 per cent.

The meal has 8–10·5 μg of thiamin/g of meal, very little active urease, and a water-soluble protein content of about 8 per cent. In nutritive value, it compared favourably with dried skim milk when semi-synthetic diets containing 15 per cent protein were fed to white rats. Indeed, weight gains were somewhat

higher on the soybean oil meal. The appearance of flakes from the desolventizer–toaster is different from the flakes from an atmospheric or from a pressure cooker. When viewed with semi-dark field illumination in a microscope (Fig. 5), particles of flakes from the desolventizer–toaster appear as if illuminated from within, i.e. they are translucent; the particles from the atmospheric and pressure cookers are translucent only at the edges. The desolventizer–toaster is now in commercial use at a number of plants, indicating the industry's recognition of the operating improvements which are effected.

B. Flash desolventizing

One of the problems in the processing of soybean flakes for use in special products is the production of undenatured meal. The vapour-phase desolventizer using

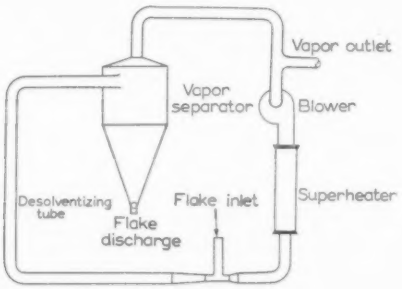

Fig. 6. Diagram of flash desolventizer.

superheated solvent vapour was developed by Leslie, and it has been used commercially for a number of years. Its primary function is to remove solvent in the production of meal for feed. Although useful in producing undenatured flakes, certain limitations do not permit a rapid removal of the solvent. In order to minimize the entrainment of fines, it is necessary to limit linear vapour velocity within the equipment. This limitation necessitates a retention time of 5 min or more in the equipment. As long as the temperature is held below 170°F, solubility of the protein is not appreciably reduced. However, when the temperature goes above 170°F, some reduction in solubility does occur. At this and slightly higher temperatures, the retention time is most important.

One method of removing the solvent from the flakes in a matter of seconds has been described by Belter and co-workers (1954). It is the comparatively simple flash-desolventizing system illustrated in Fig. 6. It consists essentially of a blower, solvent superheater, conveying and desolventizing tubes, and a cyclone. Solvent-laden flakes are pushed from their inlet tube to the cyclone by the rapidly moving vapour of the superheated solvent. The superheated solvent vaporizes the solvent in the flakes and carries the flakes to the cyclone. A suitable condensing unit must be used to recover the solvent and to return the amount of solvent evaporated from the flakes to the extracting system. Table 4 shows data on vapour and flake temperatures, solvent and moisture contents,

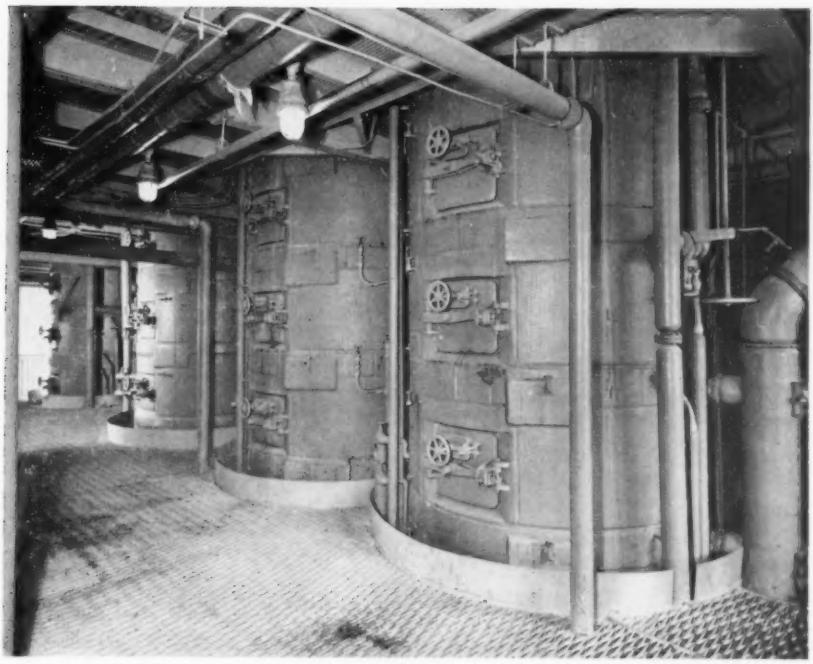

Fig. 4. Desolventizer–toaster showing three of the seven steam-jacketed compartments. (Courtesy of Central Soya Company, Inc.)

Fig. 5. Microscopic study of soybean flakes; semi-dark field illumination of 9× with particles from desolventizer–toaster at the upper left; atmospheric toaster at the upper right; and pressure toaster at the lower centre. (Courtesy of Central Soya Company, Inc.)

(*To face page 66*)

and the loss in nitrogen solubility. Although this has been used only in pilot-plant studies, it would appear that this procedure is likely to become a commercial operation as the demand for special products from soybean increases. The retention time of 2–4 sec in this equipment is the key to high nitrogen

Table 4. Effect of flash desolventizing on loss of nitrogen solubility

Original solubility (%)	*Temperature* (°F)			*Solvent in flakes* (%)	*Loss of solubility* (%)
	Vapour		*Flakes*		
	Inlet	*Outlet*			
66·1	290	260	183		0·4
63·8	329	281	191	0·36	1·8
70·3	322	286	221	0·74	0·5
68·4	322	290	215	0·20	3·0

solubility. At an exit temperature of 221°F, less than 1 per cent of nitrogen solubility is lost when flakes having 70 per cent nitrogen solubility are desolventized.

C. Cost of processing soybeans

On many occasions during the past several years, it has been reported that processors of soybeans were forced to cease operations because the cost of the beans plus the cost of processing was considerably more than the value of the meal and the oil. Indeed, the representatives of one company indicated that their special products were all that permitted them to operate profitably during many periods when other companies were shut down. The fat surplus resulting from the production of animals and cottonseed as well as soybeans, on the one hand, and the demand for soybeans for foreign trade, the availability of much storage space for soybeans, and the Government support price on the other, have been factors responsible for inconsistencies in the prices of soybeans and the return to the American processor from the products. Consequently, the National Soybean Processors Association asked the Department of Agriculture to undertake a research project to analyse data collected from the soybean processors. As a result, processing costs of a number of different soybean oil mills were collected in 1951–52 and 1952–53 (Spilsbury, 1954).

The study indicated that the average cost of processing one bushel of soybeans was 37·6 cents in 1952–53. Table 5 gives a breakdown of these costs by size of the processing operation. Note that when the size of the operation is small, labour, salaries and depreciation constitute almost a third of the total, whereas in the medium-sized and larger operations they constitute much less than a third of the total cost.

Despite the disposal of large amounts of cottonseed oil stocks to foreign buyers in 1954–55, many of the soybean processing plants were closed down from time to time because of unfavourable price relationships. The cottonseed

oil in storage may have had a depressing effect upon the market but the market did not improve substantially with the loss of these stocks. However, the bumper crop of soybeans for the 1954 crop year undoubtedly was a major factor in the failure of the soybean prices to rise during the winter and spring months

Table 5. Cost of processing soybean in cents per bushel

Item	*Bushels processed per mill during season*—1952			*Average*
	1,000,000 *or under*	2,000,000 to 3,500,000	3,500,000 to 5,000,000	
Acquiring beans	6·3	4·0	3·8	4·3
Operation				
Labour	9·1	6·2	5·0	6·2
Power and lights	1·8	2·1	1·2	1·5
Fuel and steam	1·8	1·8	2·1	2·1
Maintenance	2·4	2·0	1·6	1·5
Solvent	2·4	1·2	1·0	1·2
Total	19·0	12·2	11·9	12·8
Fixed and general				
Salaries	4·4	2·4	1·9	2·6
Depreciation	4·2	3·0	2·6	3·2
Administration	2·0	2·0	2·9	2·6
Total	19·0	12·2	11·9	12·8
Sales and packaging	4·4	3·2	3·6	4·0
Total processing costs	49·1	36·5	34·1	37·6
Coverage bushels	4,000,000	31,000,000	32,000,000	123,000,000

of 1954–55, and the storage of soybeans on the farm and in the country and terminal elevators kept much of this crop off the market, so that there was no substantial drop in the price of soybeans in the fall market.

With oil prices averaging slightly more than 10 cents/lb, meal at $50–$70/ton and bean prices at $2.50/bushel or higher, it is readily seen how some of the processors were forced to shut down until more favourable prices were available. Average spread for processing or converting a bushel of soybeans for the first 7 months of 1954 was $0.17. Only the really efficient plants could operate successfully when the average cost of processing one bushel was $0.37.

VII. Edible Soybean Oil

A. Refining

Among the recent advances made in refining of vegetable oils in the United States are use of pressure in centrifugal separations, continuous counter-current vacuum bleaching, and use of cavitation to increase the reaction of alkalis with impurities. It appears that all three of these developments could be

installed in the same plant, since they represent advances which apply to somewhat different parts of the refining operations.

One of the important considerations in the handling of any vegetable oil is oxidation. It can be difficult to trace, and with soybean oil it can lead to an inferior final product. In standard equipment available in 1950, the separation of the phosphatides from the oil in the degumming operation and the removal

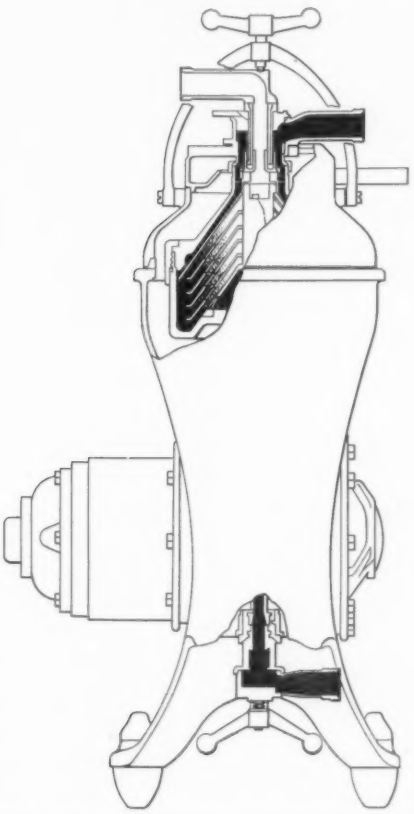

Fig. 7. Sectional view of pressure separator. (Courtesy of De Laval Separator Company.)

of soapstock from the caustic or soda ash refining step were performed in the presence of air. Indeed, the stirring during some of the processing and the high-speed centrifugation increased the exposure of the oil to oxygen of the air. By operating in a separating centrifuge designed for pressure (Fig. 7), it is possible to use nitrogen to reduce this oxidation (SULLIVAN, 1954). The oil mixture enters the separating bowl through a hollow driving spindle. Specially designed sealing devices are used at this inlet as well as the outlets for oil and gums or soapstocks. The centrifugal force effects a separation of the oil from impurities because of their difference in density. In conventional open centrifuges,

the location of the neutral zone (the zone between the two phases) depends primarily on the difference in gravity between the two phases and the diameter of the heavy phase outlet. One major improvement is the device used to regulate the diameter of this neutral zone. Instead of discharge rings on the heavy phase outlet, which could only be changed by shutting down the machine (old style), a simple calibrated pressure valve on the oil or light phase outlet can be changed

Table 6. Pressure refining

Extracted	*Crude analysis*			*Total refining loss (%)*	*Saving compared with cup (%)*
	Free fatty acid	*Wesson loss (%)*	*Cup loss (%)*		
Degumming + caustic	0·62	2·30	4·5	2·98	33
Soda ash	0·6	2·30	4·5	3·0	34
Ammonia	0·8	2·20	4·1	2·9	29

while the centrifuge is still operating. With increase back pressure of oil the neutral zone moves out; with decrease pressure it moves in. This pressure adjustment, particularly to higher pressures, makes the discharge of soybean phosphatides (gums) or heavy soapstock comparatively easy.

The pressure separator can be used easily with alkali or soda ash, and a change from one to the other can be made quickly. For caustic or alkali refining 20°–24° Be′ lye is most satisfactory. The amount of lye used should be 0·05–0·1 per cent NaOH in excess of that required to neutralize the fatty acid. With this strong lye, it is necessary to use a separate water flush to dilute the heavy phase. This water enters the bowl separately from the oil feed and washes the bowl wall without mixing with the incoming oil and caustic. If this is not done, the heavy soapstock will block the soapstock discharge and put soap into the oil phase. When the separate water flush is used, it is possible to refine degummed soybean oil with a total refining loss only 0·1–0·2 per cent greater than the theoretical Wesson loss (Sullivan, 1955).

In addition to the ease of cleaning the equipment in any change-over by backwashing with hot water, no dehydration or rehydration is required when soda ash is the refining alkali. Also, pressure reduces the release of carbon dioxide from soda ash so that objectionable frothing is not encountered. In soda ash refining, some oils give superior results when they are preheated to 160–180°F and separated at 180–200°F. A typical example of the results obtained with soybean oil is given in Table 6. In degumming, gums containing over 80 per cent phosphatides (acetone-insolubles on the dry basis) have been obtained as compared to 65 per cent phosphatides in conventional equipment. With the increase of 15 per cent phosphatides in the gums, an increase in the overall yield of oil is achieved with pressure degumming. For example, in an open-type centrifuge

producing gums with 35 per cent oil, there would be about 1·08 lb of oil going to gums for every 100 lb of crude oil processed. Under pressure operation, the total gums discharged would be 2·5 lb/100 lb, with an oil content of 20 per cent or 0·50 lb. Thus, a gain of 0·58 lb of oil per 100 lb of oil or 350 lb per tank car is achieved by pressure degumming.

For miscella refining, where the partial pressure of the solvent is present, the advantage of a closed system under pressure is obvious. The pressure separator is easily adapted to new ammonia refining procedures.

B. Bleaching

Recent developments in bleaching centre around two processes, the continuous counter-current vacuum bleaching plant and the use of ultrasonics in effecting the reaction.

The main difference between continuous vacuum bleaching and the improved counter-current process lies in the advantage gained from flow of materials in the latter. Counter-current bleaching is a natural development in the industry's shift from batch to truly continuous and efficient operation. Eventually, all the major plants may be expected to adopt more continuous procedures. Change is, however, not rapid. For example, many plants still operate on a batch basis in the bleaching operation without the benefit of vacuum.

The main features of continuous counter current vacuum bleaching as outlined by Singleton and McMichael (1955) (Fig. 8) are (a) dehydration of the oil (130°F) in the lower part of process vessel by spraying into the vessel held at a reduced pressure of 1·5 in. of mercury, (b) passage of the oil through a heat exchanger, heater, and a filter press which contains partially spent bleaching earth, and into the bottom of the upper half of the process vessel for (c) treatment with clay which has been slurried with 10 per cent of bleached oil. This clay slurry (about 25 per cent clay) is sprayed into the top of the process vessel to remove air and water introduced by clay. A small amount of steam is sparged through the oil layer at the bottom of the upper half to assist in removal of air and water and to agitate the slurry. (d) This slurry is removed continuously and passed through filter and heat exchanger to storage.

Advantages of the system are reported to be improvement in quality of oil, automatic design features which make the system simple to operate, economy of operation and space, cleanliness of plant, handling of both animal and vegetable oils without intermediate cleaning, and effective bleaching of dark oils. Calculations show that direct operation in a plant with 300,000 lb capacity would cost about 12·8 cents/100 lb in the counter-current system, whereas on a comparable basis batch vacuum and batch open kettle would require 14·2 and 16·1 cents/lb, respectively. Results achieved in comparative tests with different samples of soybean oil are shown in Table 7.

C. Cavitation in the processing of soybean oil

Since 1953, there has been a small but increasing use of cavitation to aid in the refining and bleaching of soybean, linseed and other oils. Cavitation is actually a

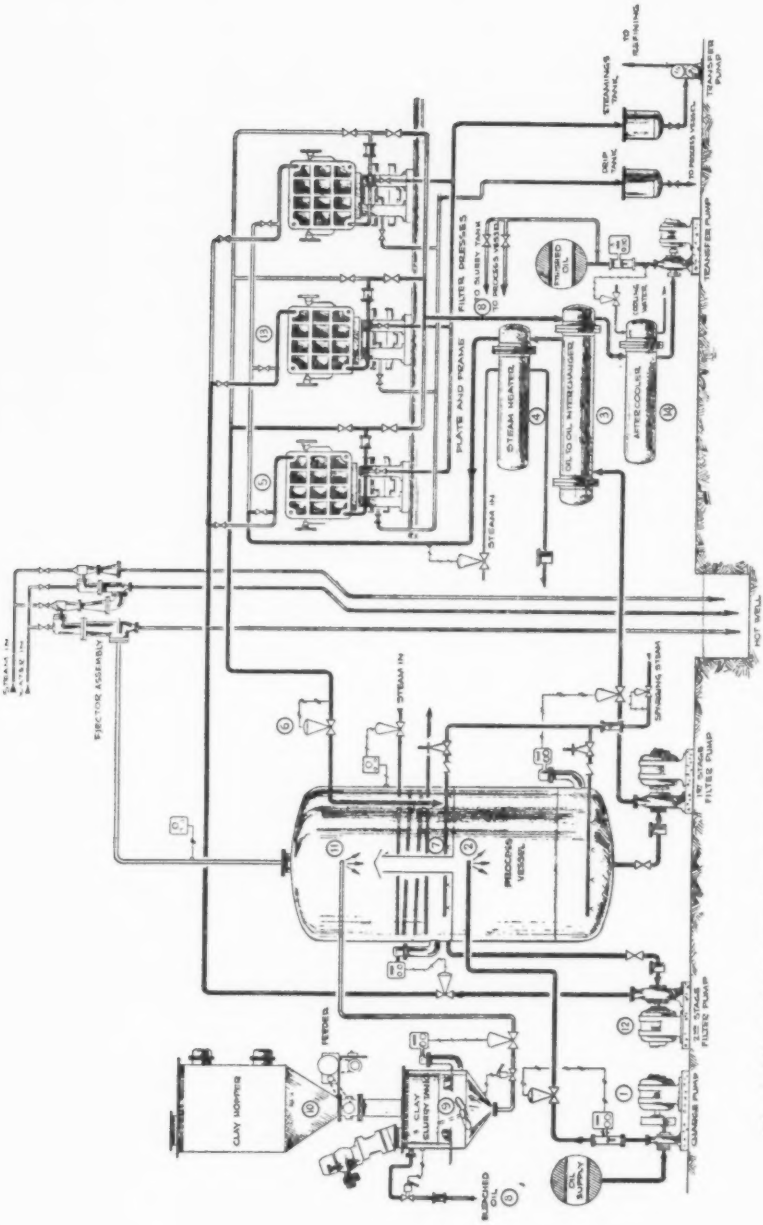

Fig. 8. Schematic diagram of continuous countercurrent vacuum bleaching system. (Courtesy of the Girdler Corporation.)

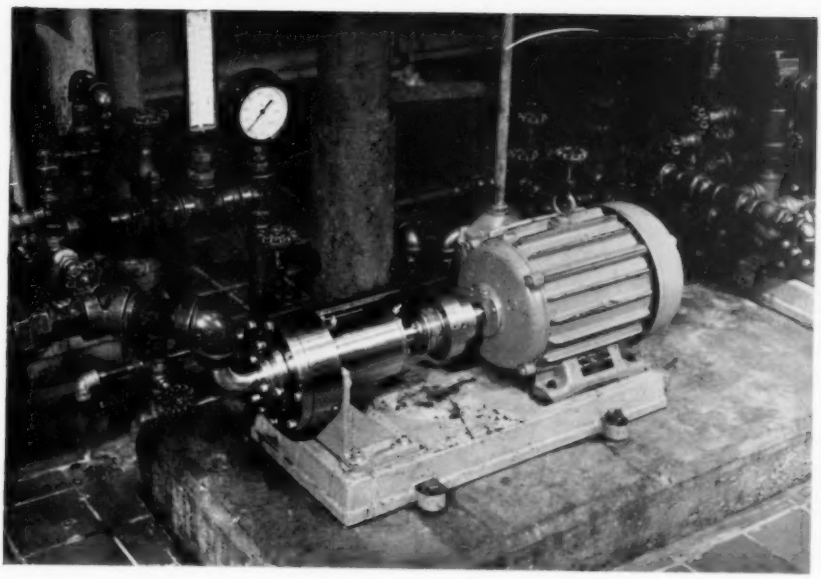

Fig. 9. Cavitation device with attached direct drive motor.
(Courtesy of Sepraton Corporation.)

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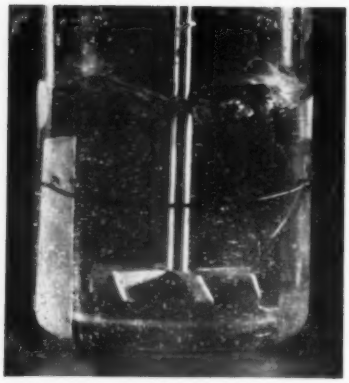
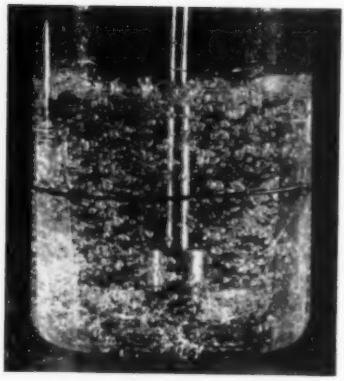
10 (a)

10 (b)



10 (c)



10 (d)

Fig. 10. Typical action of turbine and gas-dispersion agitators (laboratory scale).

phenomenon which is quite apart from any method of mixing. However, it will thoroughly mix and bring into intimate contact immiscible materials which are difficult to mix completely by other means. Examples of interest to the technology of soybeans are the contacting of alkali with oil to obtain neutral oil and

Table 7. Results of comparative tests with different bleaching processes with soybean oil

Method	% *Free fatty acids*		*Stability AOM* (h)
	Initial	*Final*	
Batch open kettle	0·12	0·15	9
Batch vacuum	0·12	0·19	11
Continuous counter-current	0·12	0·14	14

remove phosphatides, fatty acid and other materials, and of bleaching earths with the oil to remove colour. The Sepraton is a mechanical device equipped with a 5 h.p. motor (Fig. 9) which produces controlled cavitation at energy levels suitable for bulk industrial processing (Glass *et al.*, 1954). With this equipment, less alkali and bleaching earth are required to achieve comparable results. The strength of the alkali may vary without too great effect on the refining loss. Also, lower temperatures can be used in alkali refining, permitting less saponification of the neutral oil. Results which have been obtained on soybean oil are shown in Table 8. In these studies, the Sepraton replaced the

Table 8. Characteristics of refining with Sepraton

Original free fatty acids	0·6%
Wesson loss	1·9%
Cup loss	5·6%
Amount of NaOH used	1·5% of 14° Be′
% Free oil in soapstocks	27%
Actual loss	2·6%
Heat	Bleaches

conventional mixer. Actual production figures over an extended period of one year on linseed oil showed a 52 per cent saving over cup losses as compared with a 34 per cent saving over cup losses for the year previous using a conventional mixer. Ten per cent less bleaching earth was required to achieve equivalent colour.

D. Hydrogenation of soybean oil

The relation of pressure, temperature and catalyst to the selective hydrogenation of the various fatty acids in vegetable oils has been a subject of extensive investigation by a number of workers. In general, work of the last 5 years has confirmed and extended many of the previous findings. Conditions which

favour selective hydrogenation also favour the development of *trans* isomers (Feuge *et al.*, 1951). During selective hydrogenation, migration of the double bond occurs in both directions, but it appears that migration of double bonds is more strongly pronounced in the direction away from than to the ester group (Boelhouwer *et al.*, 1953). During the course of hydrogenation with nickel catalysts, conjugation occurs when linoleates are present. Approximately 90 per cent of the oleate formed from linoleate is present as *trans* isomers. The mechanism for this reaction may be isomerization in the presence of hydrogen to give *cis–trans* conjugated isomers of linoleic acid and subsequent hydrogenation of the *cis* bond preferentially (Feuge *et al.*, 1953). Allen and Kiess (1954) have suggested that half hydrogenation-dehydrogenation occurs with oleic and linoleic acids.

A recent pilot study of agitation in relation to hydrogenation of soybean oil by Beal and Lancaster (1954) indicates that the use of a gas-dispersing type of agitator rather than the simple turbine type of agitator increases selectivity. Thus, apparently a better dispersion of the gas and a greater interfacial area of the gas–oil mixture permits more selective removal of linoleic and linolenic acids, whereas a mere higher speed of agitation does not accomplish any appreciable effect on the relative rates of reaction of the two different acids as compared with oleic acid. The comparative pictures in Fig. 10 show that the gas dispersion agitator gives much more mixing of gas and oil than the turbine type.

E. Flavour reversion of soybean oil

When edible unhydrogenated samples of soybean oil are heated in the presence of air, exposed to light and air, or are exposed to certain other conditions, objectionable off-flavours develop. Hydrogenated samples of edible soybean oil develop somewhat similar flavours but to a considerably lesser extent under similar exposures. These phenomena are collectively known as a 'reversion' in flavour. This terminology is admittedly incorrect, since flavours originally present in the crude soybean oil are not achieved, but the term has been accepted as descriptive. In shortenings and margarines, developments have reduced, but not completely eliminated, this problem so that soybean oil is now the major edible fat of the United States. However, liquid soybean oil is not generally accepted as a cooking oil although it finds extensive use in salad oils, dressings, and related items (Dutton *et al.*, 1953).

Reversion appears to be an oxidative phenomenon. Presence of trace metals accelerates the oxidation of the polyunsaturated fatty acid, linolenic acid, to give off-flavours; other factors may also be important (Dutton *et al.*, 1948). These off-flavours appear to be the oxidative cleavage products of linolenic acid: acetaldehyde, propionaldehyde, α-butenal, and α-pentenal (Kawahara and Dutton 1952). Other products are present, such as maleic dialdehyde and α-heptenal (Schepartz and Daubert, 1950; Strapf and Daubert, 1950). Hydrogenated derivatives and oxidative polymers of soybean oil give similar unsaturated aldehydes (Harrison and Daubert, 1953; Johnson *et al.*, 1953). The predominant undesirable flavour of reversion may stem from α-pentenal.

Acidic compounds such as citric, tartaric, phosphoric and many other acids are effective agents for increasing the oxidative stability of liquid and hydrogenated oil (DUTTON *et al.*, 1948). Their effect in soybean oil is, in part, a direct result of their metal-inactivating or chelating properties. Their addition to soybean oil products is fairly standard practice throughout much of the industry.

Studies have shown that organic acids having the structural formula $X(YZ)_2$ or some variation of it, where X is N, S, or O; Y is CR_2, where R is H, alkyl, or other radical; and Z is an acidic group; are metal-inactivating agents (SCHWAB *et al.*, 1953). Sorbitol and other polyhydric alcohols are also effective when heated in the oil. Phosphoric acid and many of its derivatives are also effective for inactivating metals (EVANS *et al.*, 1953). Recent work has shown that the refined soybean oil must be heated before the inactivating agent can be effective but acidic inactivators need not be heated with the oil, whereas neutral (polyalcohols) inactivators must be heated therein (Evans *et al.*, 1953). Examples of the improvement in flavour and oxidative stability which can be effected by addition of metal-inactivating agents after deodorization of the oil are shown in Table 9 (EVANS *et al.*, 1954).

Table 9. *Effect of metal-inactivating agents when added to hydrogenated oil*

Inactivator 0·1%	*Initial flavour score*	*Aged flavour score* 7 days	*Peroxide values* (*AOM*–30 hr)	*Index**
CMS acid†	9·3	8·3	11	3·6
Citric acid	8·8	6·7	18	2·2
Phytic acid	8·9	6·9	14	2·9
Phosphoric acid	9·0	5·8	14	2·9
Control av.	6·4	4·6	40	
CMS acid + 0·3 p.p.m. Fe	8·8	6·8	12	4·3
Citric acid + 0·3 p.p.m. Fe	8·4	6·6	16	3·2
Phytic acid + 0·3 p.p.m. Fe	8·8	6·6	17	3·0
Phosphoric acid + 0·3 p.p.m. Fe	8·4	5·7	16	3·2
Control + 0·3 p.p.m. Fe (av.)	5·7	4·3	51	
CMS acid†	8·9	7·7‡	1·8	25
Control†	7·7	6·1‡	45	

* Peroxide value of oil containing inactivator divided by peroxide value of control.
† Carboxymethylmercaptosuccinic acid.
‡ Liquid soybean oil (aged 4 days).

The importance of metallic impurities in relation to the flavour stability of soybean oil can hardly be overemphasized. The attainment of an initially bland flavour in liquid soybean oil is very difficult in a conventional batch deodorizer constructed of ordinary steel without the use of a metal-inactivating agent. Crude soybean oil from the bean contains appreciable amounts of iron and copper which are the most important metallic impurities. 'Native' soybean oil contains as much as 0·8 p.p.m. of iron and 0·5 p.p.m. of copper, but much smaller amounts present in edible soybean oil produce off-flavours (EVANS *et*

al., 1952). As little as 0·1 p.p.m. of iron and 0·01 p.p.m. of copper can reduce the flavour stability of soybean oil (EVANS *et al.*, 1951).

Processing of the soybeans through a modern extraction plant increases the amount of metallic impurities substantially. Iron is now of primary importance; for processors and refiners have made substantial efforts to avoid copper equipment. Table 10 shows how the metallic content of soybean oil varied at different

Table 10. *Metal contents and stability evaluations of soybean oil sampled from units of two commercial extractors*

Sample description	*Metal content* (p.p.m.)				*Stability*		
	Iron		*Copper*		*AOM* 8 h 100°C	*Flavour score*	
	Crude	*Refined*	*Crude*	*Refined*		0	4 days
Company 1							
Miscella	2·70	0·088	0·16	0·002	5·5	8·9	7·2
Falling film	3·80	0·12	0·26	0·012	1·8	8·5	7·7
Stripper	5·60	0·13	0·10	0·008	1·9	7·8	6·9
Control 176E	—	0·015	—	0·006	19·4	8·3	6·1
Company 2							
Miscella	3·55	0·077	0·21	0·011	17·8	8·9	7·0
Horizontal	4·10	0·10	0·50	0·006	11·4	8·9	6·9
Falling film	4·70	0·11	0·33	0·012	16·0	8·5	7·0
Stripper	2·10	0·11	0·28	0·009	14·7	8·7	6·9

* Peroxide value milliequivalents of peroxide per kg of fat after 8 h in the AOM test.

stages in two processing plants. Samples in each plant were taken as the oil from beans progressed through the plant. Alkali and soda ash refining reduce the amount of contaminating metallic impurities to very low but still significantly important levels. Subsequently, bleaching and particularly deodorization in vessels constructed of cold-rolled steel increase the metallic impurities. The changes which can occur in metallic impurities as the oil is refined are shown in Table 11 (EVANS *et al.*, 1952). The change in oxidative stability as indicated by peroxide level after 8 h under AOM conditions is also shown in this table. Note that metallic impurities increased substantially after deodorization in the batch equipment without inactivator (Company 2).

Presence of metal-inactivating agents, both during and after the deodorization, improves stability. Although many inactivating agents have been developed none is completely satisfactory for all uses. There is need for a non-toxic, fat-soluble, heat-stable, inactivating agent which imparts no flavour to the finished product. In margarine, certain esters of citric acid with improved fat solubility are used (VAHLTEICH *et al.*, 1951).

The development of semi-continuous deodorizers of stainless steel and nickel

Table 11. *Metallic impurities and their effect on flavour score and AOM stability of soybean oil*

Sample	*Company* 1		*Company* 2		*Company* 1		*Company* 2	
					AOM	*Score*	*AOM*	*Score*
	Fe (p.p.m.)	Cu (p.p.m.)	Fe (p.p.m.)	Cu (p.p.m.)	8 h 100°C	0–4 days	8 h 100°C	0–4 days
Crude	4·9	0·24	2·6	0·14	19	8·7 6·5	10	8·6 7·4
Refined	0·56	0·045	0·28	0·011	13	8·8 5·7	11	8·2 7·0
Washed	0·18	0·021	0·079	0·016	8	8·8 6·4	12	8·6 6·4
Dried	0·26	0·017	0·050	0·005	42	8·7 6·1	50	7·9 4·7
Bleached	0·11	0·010	0·057	0·025	53	8·8 5·3	80	6·5 3·4
Deodorized	0·13	0·027	1·50	0·026	2	8·0 6·9	69	5·0 3·5

Notes: Company 1 used metal inactivator in deodorization: Company 2 did not. For AOM tests and flavour evaluations, the commercial samples at various stages were laboratory refined, bleached, deodorized and evaluated, depending on the extent of commercial treatment. AOM. values of 8 h are peroxide values of oil. Lowest value indicates highest stability.

has permitted the production of edible oil products from soybean oil, which are bland in flavour and low in metallic impurities. Most samples from conventional deodorizers can be improved in flavour with laboratory deodorizers, but this is not true with all samples from the newer semi-continuous methods. However, addition of metal-inactivating agents to these oils from semi-continuous deodorizers still imparts improved flavour stability. Under conditions where the effect of metallic impurities is held to a minimum, bland flavour is achieved by deodorization in stainless steel with adequate steam spraying under low pressures, which can be achieved by using a steam jet air ejector with three or more stages. It appears that liquid soybean oil must receive this low-pressure and steam spraying during the first as well as the last part of the deodorization for best results.

This type of deodorization can be effected in at least two commercial deodorizers, described by Bailey (1954) and Thurman (1952). A diagram of Bailey's deodorizer is shown in Fig. 11. Although this equipment has been discussed extensively in previous publications, some repetition is worth while in this progress report. The improvements associated with metal-inactivating agents coupled with effective deodorization have not eliminated the reversion problem, but they have been a factor in the rise of soybean oil to its present position as the major edible oil of the United States. Indeed, it is now being used in amounts equal to, or greater than lard.

The deodorizer consists of five trays for holding oil while it is treated with steam, and for heating and cooling before and after deodorization. The trays are suspended entirely within the shell and are equipped with baffles, heating or cooling coils, and outlets for steam. Oil is heated with indirect steam in the

first tray while sparging steam is used to remove the air from the oil. The oil then drops in succession to the next three trays, where it is deodorized at 220–252°C or higher. The fifth tray is used for cooling the oil. The oil is retained in each tray for approximately 30 min. Deodorizers hold 2,000 to approximately 7,500 lb or more per tray, permitting an hourly production of 15,000 lb.

This equipment has a number of advantages over batch equipment which was widely used formerly in the industry. Among the obvious advantages of this system are: (a) the last of the oil is deodorized at the same vacuum as available at the top of the deodorizer and air leaks from the shell do not pass through the oil as in some equipment: (b) heat losses are reduced to a minimum because the

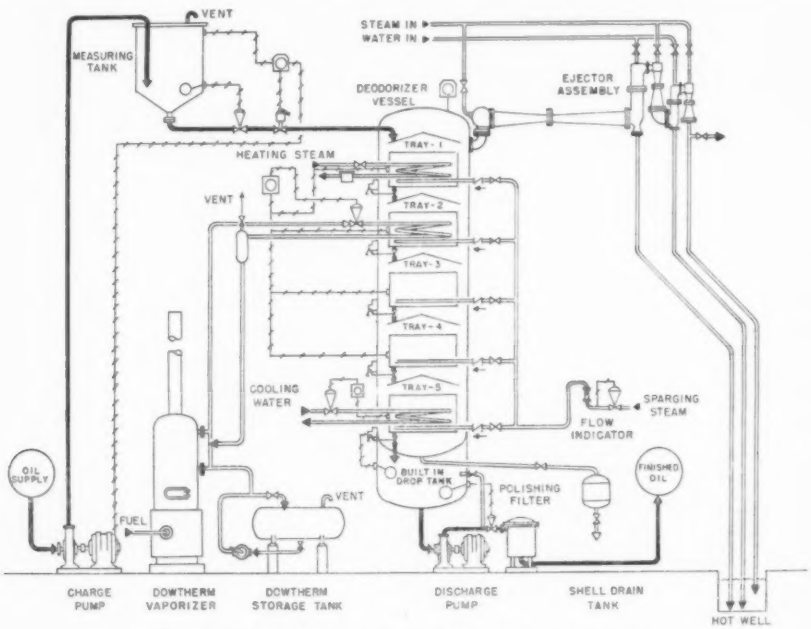


Fig. 11. Schematic diagram of semi-continuous deodorizer (Courtesy of the Girdler Corporation).

heated oil is not in contact with outer shell; (c) trays may be constructed of inert metal throughout, (d) flexibility in operation permits the use of the deodorizer on a variety of fats, and (e) time required for obtaining a good deodorization is substantially reduced.

No discussion of reversion of soybean oil would be complete without reference to THURMAN's (1952) work on deodorization of soybean oil which was concurrent with that of Bailey. It is understood that oil produced by this process was marketed as a salad oil and was a superior soybean oil. However, the marketing of this oil to the consumer was discontinued late in 1953 by the company holding the patents. A variety of reasons may have been responsible including (a) lower relative prices for cottonseed oil which replaced the soybean oil, and (b) failure

of soybean oil to perform properly as a cooking oil, particularly in deep-fat friers used in homes.

Thurman's process employed a procedure of rapidly treating comparatively small amounts of oil in a series of heaters and steam treaters. In older conventional deodorizers, comparatively large amounts of oil were deodorized in one large vertically extending still which held 30,000 lb. As described in one of Thurman's patents, each large chamber used for steam sparging and heating held approximately 2,500 lb and were horizontal extending chambers. Five chambers were employed with an hourly throughput of 7,500 lb; but large chambers would undoubtedly handle more oil per hour. The oil was heated and steam-treated in the initial chamber for 20 min to achieve a temperature of 425°F. After rapidly heating to 545°F by passage through heaters, the oil was deodorized by steam treatment at 545°F for 20 min and then passed through three more heating and steam-treating chambers until the temperature dropped to 310°F and finally to 90°F.

VIII. Other Soybean Products

A. Phosphatides

Soybean phosphatides constitute a major by-product of the soybean industry. Production and use has steadily increased during the past several years. Table 12 indicates this growth in production. Until 1945 or 1946, soybean phosphatides

Table 12. *Production of soybean lecithin in pounds*

1947	8,000,000	1951	21,300,000
1948	8,000,000	1952	20,500,000
1949	12,200,000	1953	25,000,000
1950	14,900,000	1954	26,100,000

were expensive and used in relatively small quantities. With the use of centrifuges to separate the phosphatides from the oil, production became much larger than consumption, and prices dropped to oil prices or lower. The drop in price fostered new uses. However, since phosphatides are seldom used in amounts higher than 1 per cent of a finished product, growth in use has been slow, although steady. Trading rules for soybean oil have made it attractive to leave the phosphatides in the oil to be sold for oil prices. New developments may shift the trend so that degummed oil rather than crude becomes the major article of commerce.

Granular phosphatides which are produced by acetone extraction of the oil from crude phosphatides have gained considerable use as therapeutic agents. This separation removes most of the colour from the phosphatides, leaving a white granular material containing many nutritionally important factors such as inositol, sphingolipids, lecithin, cephalin, phosphoinositides and choline. Reports indicate that many of these materials have therapeutic properties which are not attributable to their emulsifying properties (Glidden Co., 1954).

Recent investigations remove some but not all of the mysteries surrounding the composition of soybean phosphatides. In the granular phosphatides from

acetone precipitation, at least four major fractions are present: lecithin, cephalin, and two phosphoinositides (SCHOLFIELD *et al.*, 1948). The yellow colour in carefully prepared soybean phosphatides is primarily lutein, a carotene-like pigment with no vitamin A activity (SCHOLFIELD and DUTTON, 1954). The dark brown colour of unbleached soybean phosphatides is due to a brown pigment of broad absorbing capacity, characteristic of products resulting from the reaction of reducing sugars with compounds containing amino groups. The

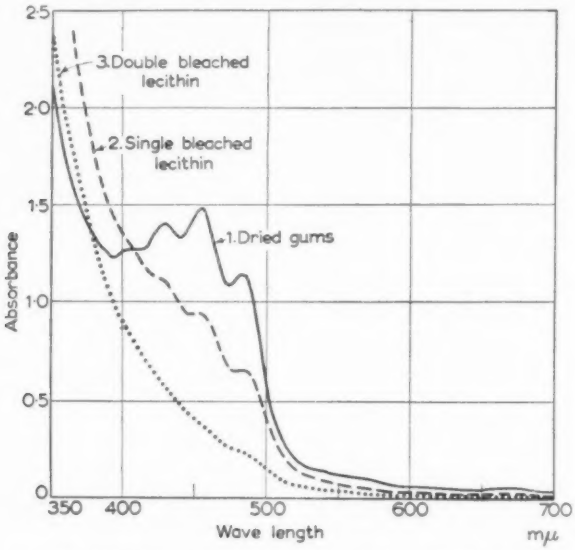


Fig. 12. Absorption spectra of lecithin solutions in CCl_4 (5 g/100 ml) measured in 1 cm in Cary recording spectrophotometer.

brown colour is produced in two places in processing: (a) in the removal of solvent from the full miscella, and (b) in the drying of the phosphatides. The lutein is readily removed by bleaching with peroxide, and peroxide substantially reduces the brown colour. Fig. 12 shows absorption spectra of lecithin solutions with the characteristic peaks of lutein in dried gums prior to bleaching. The effect of peroxide bleaching as carried out commercially is shown in the absorption curves for bleached lecithins. Fluorescence can be used to measure the amount of brown colour in the phosphatides (SCHOLFIELD and DUTTON, 1955). The relation between fluorescence and absorbance at 365 mμ, which is the minimum for carotenoid absorbance, is given by the following equation: $A_B^{365} = 0{\cdot}216 + 0{\cdot}01313F$, where A_B^{365} is the absorption at 365 mμ, and F is the unit of the scale reading for fluorescence in a Coleman 12*A* electronic photofluorometer using *B*-1 and Pc-1 filters supplied for thiamin assay.

B. Polyamide resins

One of the major uses for soybean oil in protective coatings is in alkyd resins. Here the satisfactory performance of soybean alkyds for interior finishes (good

colour retention) and their excellent outside durability have made them ingredients of many high-quality products. Although dimeric fat acids are useful in alkyds (COWAN and FALKENBURG, 1943), the more important recent developments in alkyds are thixotropic coatings based on polyamide resins containing dimeric fat acids (FALKENBURG *et al.*, 1945). WINKLER (1953) has shown that polyamide resins can be reacted with alkyd resins, varnish ester bodies, natural ester oils, and synthetic ester oils to give a vehicle for a 'gelled' product. Winkler describes the preparation of a 'gel' vehicle for a pentaerythritol alkyd: 1,125 parts of refined soybean oil (alkali-refined grade) are heated to 500°F and 310 parts of pentaerythritol and 0·5 part of litharge added. The reaction mixture is

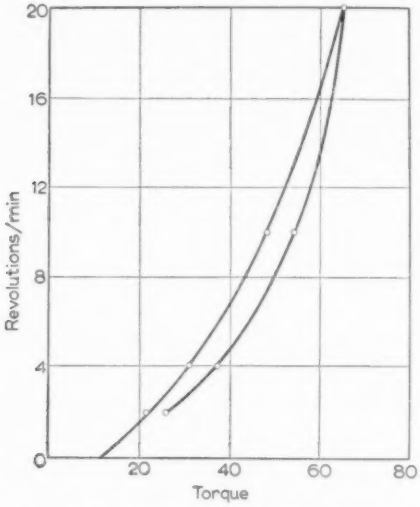


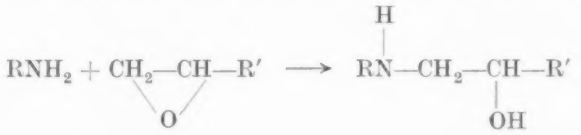
Fig. 13. Viscosity of gel of alkyd modified with polyamide resin dissolved in hydrocarbon solvent. (Courtesy of the T. F. Washburn Company.)

held at 460–470°F to complete the alcoholysis reaction as shown by solubility of 1 part of mixture in 4 parts of methyl alcohol. Add 540 parts of phthalic anhydride and heat to 480°F until an acid number of 10 or less and Gardner–Holdt viscosity of *Z* at 70 per cent solids in mineral spirits are achieved. Add 36 parts of polyamide resins, hold at 430–450°F until a cloud test, using 1–9 parts of mineral spirits, shows no graininess and has maximum turbidity. Reduce to the desired solids content with mineral spirits. This product is suitable for use in flat, eggshell, and semi-gloss paints, and as a modifying agent in enamel, semi-gloss, eggshell, and flat paints.

The thixotropic nature of the paints is shown in the typical hysteresis curve in Fig. 13. This curve was made with a Brookfield viscometer using an alkyd resin vehicle containing approximately 5 per cent polyamide. The important property of these paints is their thixotropic nature, which means that a reasonably careful 'do it yourself' painter can cover a whole room with paint without any drips on the furniture or sags on the wall. Indeed, it is possible to throw

paint from the end of a paint brush on to the wall without damaging the carpet or floor with any paint.

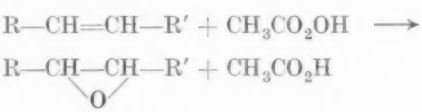
Another development based on polyamide resins is their combination with epoxy (Epon) resins (FLOYD *et al.*, 1953). The resins obtained by the reaction of ethylene diamine or other diamines with polymeric fatty acids alone or in combination with other dibasic acids possess a wide range of properties (FALKENBURG *et al.*, 1945). They may be hard and high melting or sticky and low melting. If they are prepared with a slight excess of diamine, the amine groups are present at the end of the chains and will react readily with epoxy groups. Likewise, free carboxylic acid group on the ends of chains will react as follows:



If R and R′ are polymeric, i.e. polyamide resins and epoxy resins, the reaction effectively increases the molecular weight of the polymer. Since the resins are polyfunctional, cross linking to give insoluble products can be achieved. Thus, when a low-melting polyamide resin is mixed with varying amounts of an epoxy resin, products ranging from very flexible, to hard and rigid materials are obtained. After mixing the polyamide with epoxy resins either in melt form or in solvent, the temperature determines the rate of reaction. Flexible, scuff-resistant finishes for paper, metal and many other materials are readily obtained (PEERMAN *et al.*, 1954). Gelation time will vary from a few minutes to several days. Moulded products of high impact strength suitable for mallet heads, varnishes of high gloss and good flexibility with unusual hardness, and adhesives which readily bond glass to glass and metals to glass are among the potential products. GERSON (1955) indicates that these epoxy–polyamide combinations may prove to be useful in protective coatings for automobiles.

C. Epoxy soybean oil

One of the major advances made in plasticizers for vinyl resins in recent years has been the commercial exploitation of the epoxidation of fats. The first commercial expoxidized fatty products were made from soybean oil, but in 1955 at least three other epoxy plasticizers were available: butyl, hexyl, and octyl epoxy stearate. The reaction is effected by the use of hydrogen peroxide to give peracids, such as peracetic and performic acids, which oxidize the unsaturated bond to give an epoxy derivative.

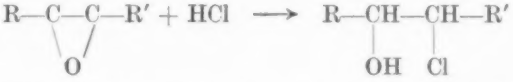


The recent basic work on this reaction by Swern and coworkers (FINDLAY, SWERN and SCANLAN, 1945) has led NIEDERHAUSER and KOROLY (1949),

GREENSPAN and GALL (1953) and others to become interested in commercial exploitation. The availability of hydrogen peroxide at low cost and the plasticizing and stabilizing properties of these fatty epoxides made commercial use almost certain.

Catalysts are not necessary with formic acid, and the reaction can be run *in situ*. Oil or ester is dissolved in formic acid using a saturated solvent, if necessary, and hydrogen peroxide added with stirring. The peracid of acetic acid can be prepared separately or prepared in the reaction mixture using a strong acid catalyst such as an ion exchange resin.

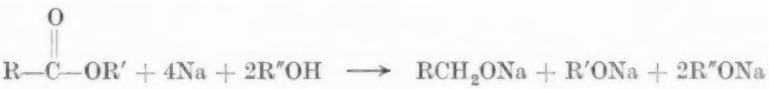
Vinyl chloride polymers and copolymers gradually decompose, particularly when hot or exposed to sunlight, to give hydrogen chloride. The decomposition is autocatalytic since hydrogen chloride accelerates the reaction. The epoxy compounds stabilize the polymer by absorbing hydrogen chloride, and this reaction is illustrated as follows:



Polymers plasticized with dioctyl phthalate have poor heat stability alone, but have excellent heat stability when they contain epoxy soybean oil. The phthalate-containing vinyl films darken considerably in 15–45 min, whereas the epoxy-containing films show little or no darkening after 45 min at 165°C. Light stability is also excellent.

D. Fatty alcohols

The surplus of fats and oils including soybean oil has led to a search for new uses for fatty materials. The reduction of fatty esters to alcohols by copper–chromium oxide for conversion to sulphates for detergents has been practised commercially in the United States since the middle 1930s. More recently, improved procedures for reducing unsaturated oils with sodium and alcohol have led to the commercial availability of soybean and other fatty alcohols. For example, the reduction of methyl linoleate gives a dienoic alcohol. Four atoms of sodium are consumed in each hydrogenation as follows:



Dilution with water forms sodium hydroxide and a mixture of alcohols. Methyl *iso*butyl carbinol or other similar alcohol is preferred to methanol or ethanol for R″OH. The sodium reduction procedure was discovered by Bouveault and Blanc in 1903, but the use of higher alcohols was developed by HANSLEY (1947) and coworkers. In 1954, the production of fatty alcohol by the sodium reduction comprised approximately 80 per cent of all fatty alcohol produced by reduction. The De Nora process using copper–chromium catalysts accounted for most of the remainder (WILSON, 1955).

The properties of a commercial sample of soybean fatty alcohol are reported to be as shown in Table 13 (ARCHER-DANIELS-MIDLAND, 1954). These properties may be varied, depending on the original oil used in the preparation and on

Table 13. *Soybean fatty alcohols*

Acid number	0·3	Flash (°F)	330·0
Saponification value	3·0	Fire (°F)	380·0
Iodine number	137·0	Specific gravity 25/25°C	0·8554
Acetyl value	186·0	Viscosity SSU/210°F	35·0
Hydroxyl value	216·0	Average molecular weight	260·0
Cloud point (°F)	59·0	Colour	White

the conditions used in the commercial operation. Soybean fatty alcohols are soluble in ethyl alcohol, *iso*propyl alcohol, benzene, naphtha, chlorinated solvents and turpentine. They can be converted to a wide variety of materials suitable for industrial use, including chain stoppers in alkyd resins and as chemical intermediates for wetting and dispersion agents and detergents. More developments are expected in the use of fatty alcohols from soybean oil, for they were made commercially available in 1955.

IX. Analyses of Soybeans

Few major changes have been made in the analytical methods for soybeans used in trading in the past several years. Detailed information about methods is given by the National Soybean Processors Association (Annual). This Association uses methods which for the most part are approved and published by the American Oil Chemists' Society (Mehlenbacher and Hopper, Annual).

A. Oil colour

Under trading rules of 1954, discounts apply when the red colour of refined bleached oil is greater than 3·5. If the colour of a green crude is light enough, no discount applies. However, if dark, a 1 or 2 per cent discount applies. Discounts are determined by comparison of samples for darkness with nickel sulphate standards, 7 and 8 g of low cobalt $NiSO_4 \cdot 6H_2O$ analytical reagent grade per 100 ml of distilled water.

Recently, the American Oil Chemistry Society tentatively adopted a new method of measuring colour involving a spectrophotometric technique. The optical density is measured at 460, 550, 620 and 670 mμ. Colour is related to the Lovibond system as follows: Colour $= 1{\cdot}29D_{460} + 69{\cdot}7D_{550} + 41{\cdot}2D_{620} - 56{\cdot}4D_{670}$ where D is optical density at indicated wavelength. This method has not proved acceptable to many analysts, since it does not always agree with the Wesson method (AOCS Cc 13B–45.) Differences are found with green oils because the spectro-photometric method does not compensate for chlorophyll to the same extent as the Wesson method (Stillman, 1953). At low chlorophyll content, the spectro-method gives a higher red-colour reading than the Wesson, whereas at high chlorophyll content, the spectro-method gives

comparatively lower red-colour readings. Table 14 shows results obtained from a study of chlorophyll contents and refined and bleached colours.

Table 14. *Effect of chlorophyll on colour of oils as measured by Wesson and spectro-methods*

	Added chlorophyll	*Wesson (Lovibond red)*	*Spectro*
Oil No. 1	0·0	7·8	8·6
Oil No. 2	3·0	6·1	3·9

STILLMAN (1953) has found that revised equations for evaluating colour and bleachability of the oil show less discrepancy between Wesson and spectro-methods: To give equivalent Lovibond red values; Colour $= 77{\cdot}4D_{550} - 31{\cdot}2D_{670}$; to give a colour value based on bleachability of the oil, Colour $= 70{\cdot}6D_{550} - 10{\cdot}7D_{670}$; and for bleached colour of non-green oils, Colour $= 4{\cdot}6D_{460} + 34D_{550}$.

A report of the OIL COLOUR COMMITTEE (1954) of the American Oil Chemists' Society indicated that eight of eighteen instruments used in a study on analyses did not meet AOCS specifications, with only two of eighteen giving results materially out of line. The committee found that use of standardizing solutions and two appropriate wavelengths might give practical methods of oil grading.

B. Oil content of soybean

Discrepancies of 0·5 per cent or more in oil content of beans have on occasion been reported from different laboratories. COLLINS (1953) showed that one major factor in these differences could be the procedures used in grinding. If the Bauer mill used in grinding the sample is permitted to heat during the grind or the beans of the sample run through rapidly, more oil can be extracted from the ground beans. When the mill was run hot (temperature of water in cooling jacket 170–180°F), the percentage of oil obtained in ten samples was 18·03, whereas when the mill run was cool (temperature of water in cooling bath 20–25°C), the oil content was 17·57. The average difference was 0·46 per cent oil in ten samples with the highest single difference 0·74 per cent. Proper use of the cooling bath and proper feeding of the beans into the mill permits reproducible accuracy of $\pm 0{\cdot}2$ per cent.

Rapid methods of analyses are useful in many commercial operations. In order to analyse beans for oil content more rapidly, HUNT *et al.* (1952) have adopted dielectric measurement to the determination of oil in beans. This method grinds the beans and extracts the oil with solvent in a Stein mill. Other mills which do not leak solvent would presumably be satisfactory. This mill is an impact cutter type with a spindle speed of 15,000 r.p.m. and blade tip speed of 135,000 in/min. Beans are ground for ½ min, and then ground and extracted with *ortho*dichlorobenzene for 4 min. The solution is filtered and

dielectric measurement made for oil content: Oil content = 14·77 + 0·09409x (x = dielectric reading). Standard error of estimate was found to be 0·27 per cent oil. One sample can be run in 15 min or 20–30 samples per hour with two analysts, two grinder–extractors, and one electronic tester. Moisture content of beans affects the values obtained. Beans having 8–12 per cent moisture give best results. Moisture content above 16 or below 7 per cent present special problems. This method had not been adopted in the industry by 1955.

C. Effects of heat treatment

A new procedure for determining the effect of heat treatment on soybean oil meal is the determination of hemagglutinating activity of the meal. During the past several years, it has been shown by LIENER (1951) and coworkers that a proteinaceous material in raw soybeans and raw soybean oil meal is toxic to certain animals. This material is destroyed by the toasting process and consequently a measure of its activity is a measure of the amount of toasting which has been effected. Fortunately this toxic material has hemagglutinating activity toward rabbit erythrocytes (LIENER, 1955). Liener has developed a photometric method of determining the hemagglutinating activity of the purified as well as crude extracts of this material. A Coleman Junior Spectrophotometer, model 6A, equipped with a special adaptor designed to hold 10 mm × 75 mm test tube is used to measure light absorption at 620 mμ. Rabbit erythrocytes which have been sensitized with trypsin are suspended in 0·9 per cent sodium chloride and mixed with dilutions of the saline extracts of soybean oil meal. Normally ten tubes containing progressive two-fold dilutions from none to 1 : 512 are used. The results of hemagglutinating activity have correlated with nutritive value as measured in the weight gains of chicks, shown in Table 15. One hemaggluti-

Table 15. *Hemagglutinating and chick growth data of soybean oil meal samples subjected to heat treatment*

Heat treatment of soybean meal (min)	*Chick weight in* 16 *days* (g)	*Hemagglutinating activity* (H.U./g × 10^2)
Atmospheric pressure*		
0 (inadequate)	90 ± 10·2	1,080
30 (inadequate)	138 ± 11·6	190
45 (inadequate)	151 ± 12·3	105
60 (inadequate	157 ± 7·1	70
75 (optimum)	172 ± 8·0	26
90 (optimum)	173 ± 9·6	24
150 (optimum)	167 ± 6·8	3
15 lb pressure		
5 (inadequate)	122 ± 12·3	296
15 (optimum)	159 ± 7·6	18
20 (optimum)	168 ± 4·7	4
30 (excess)	152 ± 8·6	0
120 (excess)	67 ± 5·0	0

* Believed to be open autoclave.

nating unit has arbitrarily been defined as that level of test solution which causes 50 per cent of the standard cell suspension to sediment in $2\frac{1}{2}$ h at room temperature. Hemagglutinating activity (x) may be calculated from the following equation with the aid of an absorption curve (not shown):

$$\log x = \log A + \frac{(E_{50} - R_A)}{(R_B - R_A)} \log 2$$

where A = reciprocal of dilution of tube nearest to having an absorption less than E_{50}, R_A = absorption tube A, R_B = absorption tube B (nearest tube having an absorption greater than E_{50}), and E_{50} is the absorption equivalent to 50 per cent of the standard cell suspension.

Another analytical method for determining the effect of heat treatment on soybean oil meal has received a good deal of attention during the past five years. When soybean oil meal is comparatively high in price, there is considerable economic pressure to add urea to the meal, particularly for cattle. Ruminants can use a diet in which approximately 30 per cent of the protein nitrogen can be replaced by urea. If the urease normally present in untoasted soybean oil meal has not been destroyed adequately, it will react with added urea, particularly in the presence of moisture, to give ammonia. Consequently, processors and feed manufacturers have explored methods of testing for this enzyme. One of the tests commonly used is the Caskey–Knapp method, which was modified by Bird and co-workers in 1947. This method has received fairly general acceptance but has not found its way into specifications or trading rules for the following reasons: The recorded differences between samples at room temperature are very small, frequent checking of the pH meter used in the method is required to prevent substantial errors, and obtaining results that check for the same meal on different days is at times difficult.

One method which is being given serious consideration for use in trading rules and specifications is the conductimetric method (Croston *et al.*, 1955). Urease converts a solution of urea with a relatively low conductivity to a solution of ammonium salts of high conductivity. In this conductimetric method it is desirable to stop the action of the enzyme immediately at the end of the reaction period. A small amount of mercuric chloride is very effective for this purpose. In this procedure control samples of buffered urea solution plus urea solutions containing the soybean meal (0·2 g of meal is preferred) are vigorously shaken and then allowed to stand at constant temperature for 30 min when the reaction is stopped. The coarse particles of meal in the solution are allowed to settle and the supernatant liquid is decanted and used for the conductivity measurement. A Leeds and Northrup portable 60 c/s conductivity bridge can be used for this purpose. Fig. 14 shows results obtained with mixtures of meals having different activities. In this figure, each meal mixture from 1 to 10 had progressively twice the activity of the mixture of the next lower number.

Other methods have been used to test for urease such as moistening of the meal after mixing 5 parts of the meal with 1 part of urea and placing in a covered jar at room temperature for 24–28 h. If a smell of ammonia develops

or Hydrion paper changes from yellow–orange to green or blue, then the meal by test contains active urease. Since this latter test is very sensitive, some feed manufacturers have adopted it to be sure that no meals containing active urease are accepted at their plants. In control of processing operations, some manufacturers use a somewhat similar test in that an indicator is placed right in the solutions of meal and urea and the colour determined after 15, 30 or more min. If test is not normal at 15 min and shows more active urease, adjustments in processing are usually made, particularly if a comparison test on the next control sample shows activity.

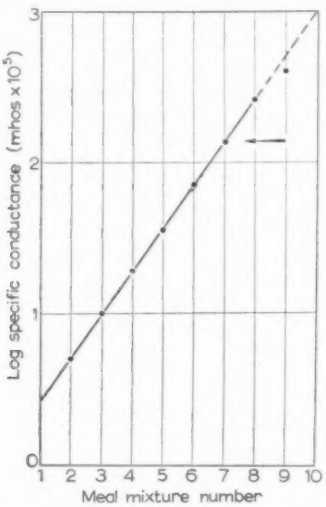


Fig. 14. Increase in log specific conductance with the increase in urease activity.

X. Future Possibilities

The record production of soybeans in the United States and the world in 1954 and 1955 indicates that the importance of this oilseed is still increasing. With increases in population and demands for livestock feed and high-quality vegetable protein products for human food, the position of soybeans in our overall economy will be considerably strengthened. Even now, the soybean processing industry is one of the major processing industries dealing with agricultural commodities. It is most likely that the production and processing of soybeans will continue to increase in volume. The use of the oil for edible purposes is likely to increase mainly as an increase in population occurs, or as the amount of other edible fats is reduced. Expansion of the use of the oil in industrial products appears likely as long as surplus fats and oils are available in United States. Trends in the protective coating industry point to increased use of alkyd resins containing soybean oil, and research will undoubtedly lead to new products just as the last 5 years have yielded a number of new fatty products from soybean oil.

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4

OILSEED RESIDUES

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OILSEED RESIDUES

*Carl M. Lyman**

I. Chemical Composition

A. Amino acid content

Although oilseed meals are important sources of industrial protein, the greatest use for these products continues to be as protein supplements in farm rations. Oilseed meals contain carbohydrates, fats, minerals, vitamins and other nutrients besides protein, but they are purchased and used primarily on the basis of their protein content. The quality of the protein as reflected by amino acid composition is of little concern to the producer of beef cattle or sheep. This is due to the capacity of the micro-organisms of the rumen to tear down dietary protein and rebuild it according to their own nutritional needs. Later the micro-organisms die and their cellular protein is digested and utilized by the animal. In marked contrast, poultry and swine must depend strictly on the amino acids contained in the diet for the building blocks from which their body protein is made. Hence, protein quality in oilseed meals is of vital concern to the producer of swine and poultry. The content of the ten essential amino acids in the various meals as determined by microbiological assay at the Texas Agricultural Experiment Station (Lyman *et al.*, 1956) are given in Tables 2 to 11.

For the purpose of calculating rations which contain given amounts of amino acids, the percentage of amino acids in the samples is given. When the object is to compare the quantitative distribution of the amino acids in the protein of different kinds of materials, it is necessary to express the data on a constant nitrogen basis. The data may be expressed as a percentage of the crude protein which amounts to the same thing as calculating to 16 per cent nitrogen. It is generally recognized that all proteins do not contain exactly 16 per cent nitrogen. However, exact figures have not been established in all cases and uniformity of treatment seems desirable. For this reason the factor 6·25 has been used for all materials reported in Tables 2 to 11.

The quantitative requirements of animals for amino acids can be expressed in several ways, the most frequent being either as a percentage of the diet or as a percentage of the protein contained in the diet. Table 1 shows the amino acid requirements of chicks and young pigs given in the latter form. In some cases the data recorded in the original literature as percentages of the diet have been recalculated for this table. Although the latest reports have been used, it is

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Table 1. *Amino acid requirements of pigs and chicks expressed as a percentage of the protein in the diet*

Amino acid	*Requirement of pigs*	*Reference*	*Requirement of chicks**	*Reference*
Arginine	—	—	6·0	Almquist and Merritt (1950)
Histidine	1·54	Mertz *et al.* (1955)	0·75	Almquist and Grau (1944); Almquist (1947)
*iso*Leucine	3·2	Brinegar *et al.* (1950a)	3·0	Grau and Peterson (1946)
Leucine	4·6	Mertz *et al.* (1955)	7·0	Grau and Peterson (1946)
Lysine	5·5	Brinegar *et al.* (1950b)	4·5	Grau *et al.* (1946); Almquist and Mecchi (1942)
Methionine	2·0†	Becker *et al.* (1955a)	2·25†	Almquist (1952); Bird *et al.* (1954)
Phenylalanine	3·6‡	Mertz *et al.* (1954)	4·5‡	Almquist and Grau (1944)
Threonine	3·0	Beeson *et al.* (1953)	2·25	Grau (1949)
Tryptophane	0·75	Becker *et al.* (1955b)	1·0	Almquist (1952)
Valine	3·1	Jackson *et al.* (1953)	4·0	Grau and Peterson (1946)

* Recalculated from original literature on the basis of 20 per cent protein chick diets.
† Additional methionine is required if the diet is low in cystine.
‡ Additional phenylalanine is required if the diet is low in tyrosine.

anticipated that further refinements in procedures will result in some modification of these values in the future.

In order to determine whether a given foodstuff is adequate or inadequate with respect to its content of any one of the essential amino acids, the requirements given in Table 1 may be compared directly with the data on amino acid content expressed as a percentage of the crude protein. For example, the requirement of a young chick for lysine is 4·5 per cent of the dietary protein. It is assumed that the chick diet will contain 20 per cent protein which is close to the average protein content of good chick feeds as used today. The lysine content of babassu meal is 4·31 per cent of the crude protein. This is 96 per cent of the chick requirement. In Table 2 this is recorded as —4 per cent indicating a deficit of 4 per cent. The value for the valine content of babassu meal given in Table 9 is 5·24 per cent of the protein which is 131 per cent of the chick requirement. This relationship is expressed as +31 per cent.

In the unusual case where a product is very poorly digested, with resulting low amino acid availability, evaluation on the above basis does not tell the whole story and consideration must be given to the proportion of the protein which is digestible.

1. *Lysine* (see Table 2).

Lysine, methionine and tryptophane are the three amino acids which are most likely to be deficient in rations for poultry and swine. Many of the oilseed meals are deficient in lysine, and this deficiency is emphasized by a general lysine deficiency in the common grains which are fed with the meals. Soybean meals

Table 2. Lysine in oilseed residues

Product	*Lysine content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	0·98	4·31	−5	−22
Castor flour	2·20	3·38	−24	−39
Castor pomace	1·20	3·02	−33	−45
Copra meal	0·68	3·06	−32	−44
Corn germ meal	1·19	5·24	+17	−5
Cottonseed meal	1·67	4·20	−7	−24
Grain sorghum germ meal	0·86	3·98	−12	−28
Linseed meal	1·33	3·62	−20	−34
Palm kernel meal	0·66	3·44	−23	−37
Peanut meal	1·38	3·53	−21	−36
Safflower meal	0·60	2·71	−40	−53
Sesame meal	1·27	2·76	−39	−50
Soybean meal	2·79	6·17	+37	+12
Sunflower seed meal	0·80	3·81	−16	−31
Tung meal	0·87	4·17	−8	−24
Walnut oil meal	0·28	2·15	−52	−61
Wheat germ meal	1·84	6·55	+46	+19

and the grain germ meals from corn, wheat and sorghum are considerably higher in lysine than most of the other oilseed meals, but still contain less lysine than fish meals (herring meal 8·2 per cent of the protein) and animal protein concentrates (tankage 7·2 per cent of the protein). It is of interest that the germ proteins of the common grains are higher in lysine than the proteins of the other parts of the seeds.

2. *Methionine* (Table 3).

Practically all the oilseed meals are deficient in methionine for the chick and the majority are deficient in this amino acid for pigs. Sesame meal is a notable exception. Unfortunately, sesame meal is quite deficient in lysine. This, together with the fact that only small amounts of sesame meal are available on the market, limits the possibility of extensive use of this product to correct methionine deficiencies in farm feeds.

3. *Tryptophane* (Table 4)

With very few exceptions the oilseed meals are good sources of tryptophane and quite a number of them contain sufficient tryptophane to compensate for

Table 3. Methionine in oilseed residues

Product	*Methionine*		*Deviation from requirement of chicks** (%)	*Deviation from requirement of pigs** (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	0·53	2·33	+4	+17
Castor flour	1·16	1·78	−20	−11
Castor pomace	0·58	1·46	−36	−27
Copra meal	0·35	1·59	−29	−20
Corn germ meal	0·43	1·90	−16	−5
Cottonseed meal	0·59	1·49	−33	−25
Grain sorghum germ meal	0·35	1·62	−28	−19
Linseed meal	0·61	1·66	−27	−17
Palm kernel meal	0·41	2·14	−4	+7
Peanut meal	0·41	1·04	−54	−48
Safflower meal	0·34	1·54	−31	−23
Sesame meal	1·22	2·65	+19	+32
Soybean meal	0·63	1·39	−38	−30
Sunflower seed meal	0·46	2·19	−1	+10
Tung meal	0·47	2·24	0	+12
Walnut oil meal	0·16	1·23	−44	−38
Wheat germ meal	0·46	1·64	−27	−18

* Additional methionine is required if the diet is low in cystine.

Table 4. Tryptophane in oilseed residues

Product	*Tryptophane content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	0·24	1·06	+6	+41
Castor flour	0·93	1·43	+43	+91
Castor pomace	0·44	1·11	+11	+48
Copra meal	0·21	0·94	−6	+25
Corn germ meal	0·29	1·28	+28	+71
Cottonseed meal	0·63	1·59	+59	+112
Grain sorghum germ meal	0·22	1·02	+2	+36
Linseed meal	0·64	1·74	+74	+132
Palm kernel meal	0·20	1·04	+4	+39
Peanut meal	0·47	1·22	+22	+63
Safflower meal	0·26	1·18	+18	+57
Sesame meal	0·88	1·91	+91	+155
Soybean meal	0·76	1·69	+69	+125
Sunflower seed meal	0·29	1·38	+38	+84
Tung meal	0·35	1·68	+68	+124
Walnut oil meal	0·20	1·53	+53	+104
Wheat germ meal	0·30	1·07	+7	+43

Table 5. Arginine in oilseed residues

Product	*Crude protein* (%)	*Arginine content*		*Deviation from requirement of chicks*
		In the sample (%)	*In crude protein* (%)	
Babassu meal	22·72	3·19	14·04	+134
Castor flour	65·03	8·39	12·90	+115
Castor pomace	39·79	3·99	10·03	+68
Copra meal	22·22	2·54	11·43	+91
Corn germ meal	22·69	1·51	6·65	+11
Cottonseed meal	39·61	4·38	11·02	+83
Grain sorghum germ meal	21·62	1·48	6·84	+14
Linseed meal	36·73	3·41	9·28	+55
Palm kernel meal	19·16	2·54	13·26	+121
Peanut meal	38·95	4·02	10·33	+73
Safflower meal	22·10	1·72	7·78	+30
Sesame meal	46·08	5·49	11·91	+98
Soybean meal	45·29	3·38	7·46	+24
Sunflower seed meal	21·02	1·63	7·76	+29
Tung meal	20·88	2·27	10·87	+24
Walnut oil meal	13·03	0·97	7·44	+23
Wheat germ meal	28·08	2·08	7·41	+23

Table 6. Histidine in oilseed residues

Product	*Histidine content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	0·41	1·81	+141	+18
Castor flour	1·36	2·09	+180	+36
Castor pomace	0·67	1·68	+140	+9
Copra meal	0·38	1·71	+127	+11
Corn germ meal	0·78	3·44	+360	+123
Cottonseed meal	1·73	2·70	+260	+75
Grain sorghum germ meal	0·73	3·38	+351	+119
Linseed meal	0·66	1·80	+140	+17
Palm kernel meal	0·31	1·62	+113	+5
Peanut meal	0·84	2·16	+186	+40
Safflower meal	0·44	1·99	+165	+29
Sesame meal	1·02	2·21	+193	+43
Soybean meal	1·12	2·49	+112	+61
Sunflower seed meal	0·46	2·19	+193	+42
Tung meal	0·48	2·30	+207	+49
Walnut oil meal	0·21	1·61	+113	+5
Wheat germ meal	0·64	2·28	+207	+48

Table 7. Phenylalanine in oilseed residues

Product	*Phenylalanine content*		*Deviation from requirement of chicks** (%)	*Deviation from requirement of pigs** (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	1·35	5·94	+32	+65
Castor flour	3·38	5·19	+16	+44
Castor pomace	1·86	4·68	+4	+30
Copra meal	0·94	4·23	−6	+18
Corn germ meal	0·95	4·19	−7	+16
Cottonseed meal	2·09	5·25	+17	+46
Grain sorghum germ meal	1·00	4·62	+3	+28
Linseed meal	1·65	4·49	0	+25
Palm kernel meal	0·82	4·28	−5	+19
Peanut meal	1·94	4·97	+10	+38
Safflower meal	1·16	5·25	+17	+46
Sesame meal	2·18	4·73	+6	+31
Soybean meal	2·20	4·86	+8	+35
Sunflower seed meal	1·76	5·12	+13	+42
Tung meal	1·52	7·28	+62	+102
Walnut oil meal	0·43	3·30	−27	−8
Wheat germ meal	1·11	3·96	−12	+10

* Additional phenylalanine is required if the diet is low in tyrosine.

the tryptophane deficiency of corn. Sesame meal is particularly high in tryptophane as well as being a good source of methionine.

4. *Arginine* (Table 5).

All the oilseed meals contain more arginine than is required by the chick. This is probably true for young pigs as well.

5. *Histidine* (Table 6)

No deficiency in histidine in any of the oilseed meals is indicated for either swine or poultry.

6. *Phenylalanine* (Table 7)

A few oilseed meals are borderline or mildly deficient in phenylalanine for chicks. This is of no practical significance since corn, wheat, and the grain sorghums all contain more phenylalanine than the minimum requirement. A deficiency of phenylalanine is rarely if ever encountered under practical conditions.

7. *Threonine* (Table 8)

All the oilseed meals, except walnut oil meal which to date has no commercial significance, appear to have sufficient threonine to meet the requirements of

Table 8. Threonine in oilseed residues

Product	*Threonine content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	0·71	3·13	+40	+4
Castor flour	2·50	3·84	+67	+28
Castor pomace	1·29	3·24	+44	+8
Copra meal	0·84	3·78	+69	+26
Corn germ meal	0·94	4·14	+96	+38
Cottonseed meal	1·38	3·47	+53	+16
Grain sorghum germ meal	0·74	3·42	+52	+14
Linseed meal	1·39	3·78	+69	+20
Palm kernel meal	0·60	3·13	+40	+4
Peanut meal	1·16	2·98	+33	−1
Safflower meal	0·65	2·94	+31	−2
Sesame meal	1·68	3·64	+62	+21
Soybean meal	1·82	4·03	+80	+34
Sunflower seed meal	0·72	3·43	+53	+14
Tung meal	0·96	4·60	+104	+53
Walnut oil meal	0·34	2·61	+16	−13
Wheat germ meal	1·11	3·95	+76	+32

Table 9. Valine in oilseed residues

Product	*Valine content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	1·19	5·24	+31	+69
Castor flour	4·38	6·74	+69	+117
Castor pomace	2·15	5·40	+35	+74
Copra meal	1·22	5·49	+38	+77
Corn germ meal	1·50	6·61	+65	+113
Cottonseed meal	1·98	4·98	+25	+61
Grain sorghum germ meal	1·44	6·66	+66	+115
Linseed meal	2·04	5·55	+39	+79
Palm kernel meal	1·03	5·38	+35	+74
Peanut meal	1·88	4·82	+20	+55
Safflower meal	1·09	4·93	+24	+58
Sesame meal	2·33	5·06	+26	+63
Soybean meal	2·45	5·40	+35	+74
Sunflower seed meal	1·03	4·90	+23	+58
Tung meal	1·74	8·33	+109	+169
Walnut oil meal	0·50	3·82	−5	+23
Wheat germ meal	1·41	5·02	+25	+65

Table 10. *Leucine in oilseed residues*

Product	*Leucine content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	1·40	6·17	−12	+34
Castor flour	4·16	6·40	−9	+39
Castor pomace	2·25	5·65	−19	+23
Copra meal	1·40	6·30	−10	+37
Corn germ meal	1·97	8·68	+24	+89
Cottonseed meal	2·46	6·20	−11	+35
Grain sorghum germ meal	1·88	8·70	+24	+89
Linseed meal	2·19	5·96	−15	+29
Palm kernel meal	1·23	6·42	−9	+40
Peanut meal	2·60	6·68	−4	+45
Safflower meal	1·22	5·52	−21	+20
Sesame meal	3·19	6·92	−1	+50
Soybean meal	3·48	7·69	+10	+67
Sunflower seed meal	1·25	5·95	−15	+29
Tung meal	1·58	7·57	+8	+65
Walnut oil meal	0·68	5·22	−26	+13
Wheat germ meal	1·67	5·95	−15	+29

chicks and pigs. Certain varieties of wheat are mildly deficient in threonine and it would be possible to formulate mixed rations with certain oilseed meals and wheat which would be deficient in threonine. In practical feed mixing operations this is very unlikely to happen.

8. *Valine, leucine and* iso*leucine* (Tables 9–11)

A deficiency of any of these three monoamino-monocarboxylic acids of similar structure is not ordinarily found in practical farm rations for swine and poultry. Tables 9 and 11 show that the oil seed meals are abundantly supplied with valine and *iso*leucine. Table 10 would indicate a mild deficiency of leucine in several of these products. The reason why this deficiency of leucine is of no practical significance is that corn and the grain sorghums which are so frequently fed along with the oilseed meals to poultry and swine are especially high in leucine content (corn 11·8 per cent of the protein). The requirement of the young pig for leucine is less than the requirement for chicks, and no deficiency of leucine is indicated in any of the meals when used in swine rations.

B. Vitamin and Mineral Content

Table 12 gives average values for the content of the vitamins and minerals which are of particular significance, in practical animal nutrition. These data were collected from numerous sources.

Table 11. iso*Leucine in oilseed residues*

Product	iso*Leucine content*		*Deviation from requirement of chicks* (%)	*Deviation from requirement of pigs* (%)
	In the sample (%)	*In crude protein* (%)		
Babassu meal	0·88	3·87	+28	+21
Castor flour	3·46	5·32	+77	+66
Castor pomace	1·85	4·65	+55	+45
Copra meal	0·89	4·00	+33	+25
Corn germ meal	0·96	4·23	+42	+32
Cottonseed meal	1·59	4·01	+33	+25
Grain sorghum germ meal	0·98	4·53	+51	+42
Linseed meal	1·68	4·57	+52	+43
Palm kernel meal	0·76	3·97	+32	+24
Peanut meal	1·69	4·33	+45	+35
Safflower meal	0·85	3·85	+28	+20
Sesame meal	1·97	4·27	+42	+33
Soybean meal	2·49	5·50	+82	+72
Sunflower seed meal	0·95	4·52	+52	+41
Tung meal	1·03	4·93	+65	+54
Walnut oil meal	0·42	3·22	+7	+1
Wheat germ meal	0·97	3·45	+15	+8

Table 12. *Vitamin and mineral content of oilseed residues*

Product	*Thiamine* (mg/lb)	*Riboflavin* (mg/lb)	*Niacin* (mg/lb)	*Pantothenic acid* (mg/lb)	*Choline* (mg/lb)	*Calcium* (%)	*Phosphorus* (%)	*Iron* (%)	*Manganese* (mg/lb)	*Copper* (mg/lb)	*Cobalt* (mg/lb)
Babassu meal						0·13	0·71	0·035	141·1	18·9	
Copra meal	0·3	1·2	13·3	7·3							
Corn germ meal	0·6	1·9	17·5	4·0	806	0·06	0·56	0·032	7·3	5·9	
Cottonseed meal	5·0	2·5	13·0	6·4	1525	0·2	1·22	0·008	12·9	7·7	0·06
Linseed meal	3·5	1·5	16·8	8·0	650	0·4	0·9	0·024	19·1	11·8	0·17
Palm kernel meal			20·0					0·017	90·0	13·7	
Peanut meal	2·6	1·6	96·6	24·7	1025	0·1	0·6				
Sesame meal		1·5		5·6	700						
Soybean meal	1·4	1·7	17·1	10·1	1330	0·3	0·6	0·017	13·6	11·1	0·05
Sunflower seed meal		1·4		11·0	544		0·55	0·003	9·8		
Wheat germ meal	11·8	2·4	23·5	11·5	2072	0·08	1·11	0·011	73·7	4·3	

1. *Thiamine*

The thiamine content of oilseed meals varies considerably not only because of variation in the seed, but also because of destruction by moist heat during processing. In spite of such losses, the oilseed meals are usually fair sources of thiamine. With certain processing conditions, the thiamine content may be reduced to very low levels. Wheat germ meal is an excellent source of thiamine.

2. *Riboflavin*

The oilseed meals are fair to good sources of riboflavin.

3. *Niacin*

Peanut meal is a rich source of niacin. Most of the other oilseed meals would be rated as fair sources of this vitamin.

4. *Pantothenic acid*

The oilseed meals are good sources of pantothenic acid.

5. *Choline*

The oilseed meals are excellent sources of choline. The choline content of wheat germ meal is eight to ten times that of corn.

6. *Vitamin A*

The vitamin A potency (carotene + vitamin A) of the oilseed meals is too low to be of any particular significance.

II. Factors Which Influence the Nutritive Value of Soybean Oil Meal

That a mild heat treatment during the processing of soybean oil meal increases the nutritional value of the protein is now widely recognized. Following the original report of Osborne and Mendel in 1917b, numerous investigators have studied this phenomenon which is not a general one except in beans and peas. Fortunately, the span between the minimum amount of heat which produces maximum nutritional value and the amount of heat which causes serious impairment is rather wide. Thus, the favourable effect of heat processing on the growth-promoting value of soybean proteins for chicks may be accomplished by 15 min autoclaving at 15 lb pressure (Clandinin *et al.*, 1947). Marked decrease in nutritional value occurs only after autoclaving for more than 1½h (Fritz *et al.*, 1947).

A major contribution toward an understanding of the causes of the beneficial action of heat on soybeans came with the discovery in 1944 by both Bowman (1944) and Ham and Sandstedt (1944), of a substance in soybeans which greatly retards the activity of trypsin *in vitro*. Later, Ham *et al.* (1945) showed that an extract of soybeans containing the tryptic inhibiting substance retarded the growth of chicks when included in the diet. The work was extended to rats by Klose *et al.* (1946). The trypsin inhibitor was crystallized in 1945 by Kunitz. It is a globulin with a molecular weight of 24,000 and an isoelectric point at pH 4·5. It blocks the action of an approximately equal weight of trypsin by combining with it to form a stable compound. In a later investigation on the isolation and crystallization of the inhibitor, Kunitz (1947) found that the pure compound shows neither proteolytic or inhibitor properties. When partly denatured by heat in acid solution, it exhibits tryptic activity. The

trypsin-inhibiting characteristic appears if the compound is partly denatured in alkaline solution.

An important part of the evidence concerning the nutritional significance of the trypsin inhibitor in raw soybeans was the finding that crystalline trypsin increased the growth rate of chicks fed diets containing raw soybean protein (Almquist and Merritt, 1953).

For some time it appeared that the presence of the trypsin inhibitor in raw soybeans provided a satisfactory explanation of the whole phenomenon, but later investigations have shown that the problem is more complex.

Liener (1953) found that only half of the growth retardation induced by the presence of raw soybean meal in the diet of rats could be counteracted by trypsin. Liener (1951) also observed that a crude concentrate of the soybean trypsin inhibitor caused the death of young rats when injected intraperitoneally, while the crystalline trypsin inhibitor, on the other hand, proved to be non-toxic even when injected at levels of antitryptic activity far exceeding that of the crude preparation. Subsequently, the isolation of a toxic substance from defatted soybean flour was achieved (Liener and Pallansch, 1953). This substance was named soyin. The physical characteristics of soyin as described by Pallansch and Liener (1953) are as follows: a protein of molecular weight 105,000; isoelectric point 6·1. A biological characteristic of soyin is its hemagglutinating action (Liener and Pallansch, 1953). Liener (1953) has reported that soyin preparations free of antitryptic activity inhibit the growth of rats when fed at levels comparable with those found in raw soybeans. This inhibition was not counteracted by adding trypsin to the diet. It was concluded that only about one-half of the growth retardation caused by raw defatted soybeans should be attributed to soyin. The data from Liener's report are given in Table 13. When the food intake of the animals receiving soyin was limited to that of the controls, there was very little difference in growth rate, indicating that soyin acts by causing a reduction in food consumption.

The immunochemical properties of soyin have been studied by Liener and Rose (1953). Based on these studies and hemagglutinating data, it was concluded that the soyin content of defatted soybean flour is about 3 per cent.

Lipke, Fraenkel and Liener (1954) have found a substance in raw soybeans which inhibits the growth of the larva of the insect *Tribolium confusum*. This work developed from the observation that soybeans have a natural resistance to insect infestations. It was suspected that the beans contain some substance which inhibits the growth of the pests. Of particular significance is the finding that the *Tribolium* inhibitor is not identical with soyin or the crystalline trypsin inhibitor. The inhibitor is precipitable from an extract of raw soybeans at pH 4·6, by 0·475 saturation with ammonium sulphate, indicating that the substance is probably protein in nature. Whether this inhibitor has any significance in the nutrition of chicks and rats has yet to be determined.

As the problem stands at this date, the evidence is still good that a trypsin inhibitor in raw soybeans retards the growth of animals unless it is inactivated by heat during processing or by other means. At the same time the evidence is

Table 13. *Rat growth experiments with soyin and raw or autoclaved soybean flour in the presence or absence of crude trypsin** (LIENER, 1953)

Series†	*Protein source*‡	*Supplement*	*Weight gain*		*Food intake*		*Growth inhibition* (%) ¶
			Mean§ (g)	'*t*' *value*‖	*Mean*§ (g/day)	'*t*' *value*‖	
1	Autoclaved soy	None	43·8 ± 4·2		8·0 ± 0·4		
	Raw soy	None	20·5 ± 3·7	4·23	6·4 ± 0·4	3·35	53·2
2	Autoclaved soy	None	64·3 ± 5·0		7·7 ± 0·9		
	Autoclaved soy	0·5% soyin	60·3 ± 7·1	1·23	7·6 ± 0·9	0·30	6·2
3	Autoclaved soy	None	60·5 ± 5·1		10·4 ± 0·4		
	Autoclaved soy	1·0% soyin	45·0 ± 1·1	2·72	8·2 ± 0·4	3·16	25·6
4	Casein	None	68·8 ± 3·6		9·4 ± 0·2		
	Casein	1·0% soyin	56·3 ± 1·1	4·40	8·1 ± 0·3	6·56	18·2
5	Autoclaved soy	5% trypsin	66·8 ± 5·1		9·6 ± 0·7		
	Raw soy	None	24·5 ± 8·5	11·42	6·5 ± 1·3	5·31	63·3
	Raw soy	5% trypsin	48·8 ± 11·1	2·46	8·6 ± 1·3	1·62	26·9
6	Autoclaved soy	5% trypsin	66·0 ± 2·7		9·1 ± 0·2		
	Autoclaved soy	5% trypsin + 1·0% soyin	50·3 ± 3·3	3·58	7·2 ± 0·5	3·98	23·8
7	Autoclaved soy	None	43·0 ± 5·6		8·0 ± 1·0		
	Raw soy	None	33·3 ± 5·1	9·32	8·0 ± 1·0		22·6
8	Autoclaved soy	5% trypsin	44·3 ± 5·9		7·0 ± 0·6		
	Raw soy	5% trypsin	42·3 ± 4·8	1·79	7·0 ± 0·6		4·5
9	Autoclaved soy	None	50·3 ± 1·7		8·5 ± 0·4		
	Autoclaved soy	1·0% soyin	48·0 ± 1·9	1·50	8·5 ± 0·4		4·6

* Trypsin powder (1–110), Pfanstiehl Chemical Co., Waukegan, Ill.

† In series 1–6, animals were fed *ad libitum*. In series 7–9, the food intake of the control group was restricted to that of the experimental group.

‡ The group listed first within each series constitutes the control.

§ The mean of each group (4 animals) ± the standard error of the mean over a period of two weeks

‖ Calculated according to SNEDECOR (1946) on the basis of paired comparisons between litter mates, of the same initial weight (±1 g) and sex distributed in the control and experimental groups: '*t*' values >2·45 indicate a difference from the control significant at a level of <0·05, and '*t*' values >3·71 indicate a difference significant at a level of <0·01.

¶ Percentage difference in gain in weight between control and experimental groups.

good that the trypsin inhibitor is not the only major factor involved in the beneficial action of moist heat on raw soybean protein. Since both the trypsin inhibitor and soyin are proteins, it is not surprising that both are destroyed under similar conditions. The possibility remains that there are still other inhibitors which are of significance in the heat treatment of soybean meal.

Laboratory tests have been sought which will determine when the heat treatment of soybean meal has been adequate yet not excessive. The disappearance of urease activity from the meal has so far been used most extensively. The test is based on the principle that when the enzyme urease is inactivated by denaturation other proteins will have been denatured as well. Although the urease test has been very useful, it still leaves much to be desired as a method for evaluating the adequacy of heat treatment of soybeans (BORCHERS *et al.*, 1947). The test gives no indication at all concerning overheating.

A photometric method for the determination of the hemagglutinating activity of soyin and crude soybean extracts has been described by LIENER (1955) who suggests that this method has potential value for predicting the nutritive value of soybean meals subjected to various degrees of heat treatment.

III. The Effect of Processing Conditions on the Nutritive Value of Cottonseed Meal

In the early days of cottonseed oil milling in this country the protein residue accumulating at the mills constituted a waste disposal problem. Later as the

meal began to be used extensively in cattle feeding operations, it was believed by many that cottonseed meal caused blindness, stiffness of gait, swelling of the joints and loss of appetite in cattle. Thorough investigation (REED *et al.*, 1928; HALVERSON and SHERWOOD, 1930; MOORE and HUFFMAN, 1931; KUHLMAN *et al.*, 1939. DICKSON *et al.*, 1940) showed conclusively that these difficulties were due to vitamin A deficiency and had nothing to do with the characteristics of cottonseed meal, except that cottonseed meal contains no vitamin A. When cottonseed meal is fed with poor-quality roughage, vitamin A must be supplied in some form or other.

For a number of years after the establishment of the use of cottonseed meal in cattle feeding, textbooks contained the statement that cottonseed meal contains a poisonous substance for hogs and chickens and should never be fed to these farm animals. The first break in this situation came with the report of HALE (1930) showing that commercial cottonseed meal could be safely and profitably fed to hogs if the amount was limited to 9 per cent of the diet. This conclusion was soon confirmed by other workers (LOEFFEL, 1932)

From the chemical point of view, the early work may be briefly summarized as follows: gossypol, a bright yellow compound was isolated from cottonseed by MARCHLEWSKI in 1899; WITHERS and CARRUTH (1918) and later SCHWARTZE and ALSBERG (1924) showed that purified gossypol has a poisonous effect similar to that of raw cottonseed when fed to rabbits, rats, guinea pigs and swine. During the processing of cottonseed, the moist heat treatment during the 'cooking' causes the inactivation of a large proportion of the gossypol in the meats. WITHERS and CARRUTH (1918) postulated that this inactivation was the result of an oxidative process and named the supposed decomposition product 'd' gossypol. Later CLARK (1928) showed that the chemical structure of gossypol is not altered as a result of conversion to 'd' gossypol. Solubility relationships are changed, and these were interpreted as being the result of the combination of the gossypol with some of the cottonseed protein presumably through an amino group of the protein and the carbonyl group of gossypol. Following Clark's suggestion, inactivated gossypol is often called bound gossypol. In order to study the chemical and biological significance of the reaction between protein and gossypol, gossypol–protein compounds were prepared in the laboratory by LYMAN (1948) and by CASTILLION and ALTSCHUL (1950). The chemical structure of gossypol itself proved to be a difficult problem which was solved by Adams and co-workers and reported in a series of twenty-three papers terminating in 1939 (ADAMS and GEISSMAN, 1939).

Many workers have sought ways and means of making cottonseed meal safe and satisfactory for use in diets for hogs and poultry at any level which is economical to feed. The first lead in this problem was the work of OSBORNE and MENDEL (1917) who showed that the toxicity of raw cottonseed could be progressively reduced by steaming. Following this report, the effects of treating commercial cottonseed meal by steaming, autoclaving (MACY and MENDEL, 1920; DOWELL and MENAUL, 1923; GALLUP, 1926; 1927; HASSEL, 1930) or cooking with water (OSBORNE and MENDEL, 1917a; SEWELL, 1943) were investigated. Other

historical methods which have been used to detoxify cottonseed meal include the use of soluble iron salts (WITHERS and BREWSTER, 1913; WITHERS and CARRUTH, 1917; MCGOWAN and CRICHTON, 1924; GALLUP, 1928b; ROBINSON, 1934, 1936) either to treat the meal or as additives to the diet.

LYMAN, HOLLAND and HALE (1944) showed that cottonseed meal which will not cause injury of any kind to guinea pigs or to swine even when fed at a level of 25 per cent of the diet, can be consistently produced in a typical hydraulic oil mill. The procedure is based on the control of the processing factors—temperature, time and moisture content. Such meal has a free gossypol content of only about 0·02 per cent. Unfortunately protein quality in meal prepared in this way was not generally satisfactory.

About this time it became apparent that the utilization of cottonseed meal by animals other than the ruminants involves two major factors. The first is the necessity of reducing the free gossypol content to fairly low levels in order to avoid the unfavourable physiological effects of this compound. The second factor concerns the quality of the protein as modified by processing and other variables. Cottonseed is usually subjected to some degree of heat treatment during the commercial production of the meal. The detrimental effect of heat on cottonseed protein has been shown by OSBORNE and MENDEL (1917), GALLUP (1928a), and OLCOTT and FONTAINE (1941).

More recently KUIKEN and LYMAN (1948), and KUIKEN (1952) showed that only part of the lysine in commercial cottonseed meal and flour is available for utilization by the rat. It was also found that lysine availability varies according to the processing conditions. Table 14 shows the lysine availability of

Table 14. *True availability of amino acids in cottonseed flour, peanut flour and wheat* (KUIKEN and LYMAN, 1948)

Amino acid	*True availability**		
	Cottonseed flour (%)	*Peanut flour* (%)	*Wheat* (%)
Arginine	93·4	99·5	96·4
Histidine	89·9	98·8	98·8
*Iso*leucine	78·2	97·2	95·0
Leucine	75·4	97·0	95·4
Lysine	64·5	97·0	92·8
Methionine	81·6	95·8	94·9
Phenylalanine	88·6	97·9	96·9
Threonine	76·6	94·8	92·2
Tryptophane	90·8	97·2	93·2
Valine	78·6	95·8	93·2
Total nitrogen		97·7	95·0

* Average values based on groups of five animals each.

a sample of cottonseed flour as compared to peanut flour and wheat. In this particular sample of cottonseed flour only 65 per cent of the lysine was available while at the same time almost all of the arginine was available. This might be

expected if the ϵ amino group of lysine were tied up by reaction with gossypol. A particularly significant finding was that lysine availability was sharply reduced by heating cottonseed protein in the presence of both gossypol and cottonseed oil. Heating the protein alone, with gossypol in the absence of oil, or with oil in the absence of gossypol had little effect on the availability of lysine. It seems probable that the function of the oil was to dissolve the gossypol and bring it into contact with the protein. These findings indicated that gossypol is involved in the reduction of lysine availability in cottonseed meal. The lowered lysine availability which occurs when certain proteins are heated alone appears to be due to a different type of reaction.

Following this work, a collaborative study was conducted on cottonseed meals of known processing history by a number of research groups. Each group selected the type of tests best suited to their interest and facilities. The meals were prepared by the hydraulic, the screw press, the pre-press solvent, and the solvent manufacturing processes.

They were collected and distributed by the Southern Regional Research laboratory of the U.S. Department of Agriculture. The collaborators were agreed at the end of the first series of tests that cottonseed meal made by any process varies in nutritional value over a wide range depending on the processing conditions. It was further agreed that a chemical test for evaluating the quality of the protein in the experimental meals was badly needed. Previously the solubility of the protein of cottonseed meal samples in dilute sodium chloride solution had been proposed by Olcott and Fontaine (1942) as a means to determining when meals had been overlooked. In limited series of meals this sometimes gave good results, but as the collaborative data accumulated there were far too many meals which did not fit the pattern.

In a report on the collaborative meals by Lyman *et al.* (1953) it was found that a relationship existed between protein quality, as indicated by chick feeding tests in which cottonseed meal was the sole source of protein, and the solubility of the nitrogen in 0·02N sodium hydroxide. These tests were made at the suggestion of Dr. Raymond Reiser who had previously studied the peptization of soybean protein in overheated soybean oil meals (Reiser, unpublished). A relationship was also found between bound gossypol and protein quality. Based on these two relationships a formula was proposed for calculating a chemical index value for the meals. Later it was realized that bound gossypol and nitrogen solubility in 0·02N sodium hydroxide are not independent variables and solubility in 0·02N NaOH alone is a good indication of protein quality.

Table 15 shows the wide variation which was found in the nutritional value of the meals and also shows that poor lysine availability is a major factor in the poorer meals because the growth of the chicks was more than doubled by adding lysine to the diets. The percentage increase obtained by lysine supplementation in the case of the better meals was much smaller.

Table 16 shows the results of a later collaborative test on pre-press solvent cottonseed meals in which the above chemical tests were applied. The relationship between protein quality and gossypol and between protein quality and

Table 15. *The effect of lysine supplementation on the nutritional value of cottonseed meals for chicks* (LYMAN *et al.*, 1953)

Cottonseed meal no.	*4-week gain**			*Gain/feed ratio*	
	Without lysine (g)	*With lysine* (g)	*Increase with lysine* (%)	*Without lysine*	*With lysine*
25	101·8	236·8	132·6	3·95	2·80
20	111·4	258·3	131·8	3·98	2·85
29	125·7	277·2	120·5	3·38	2·59
24	124·6	241·1	93·5	3·29	2·33
19	144·3	282·1	95·5	3·40	2·52
9	153·6	218·0	41·9	3·20	3·02
17	155·3	239·8	54·4	3·22	2·72
14	207·0	253·3	22·3	2·79	2·47
10	210·3	260·0	23·8	2·63	2·36
16	220·2	261·9	18·9	2·71	2·70
Soybean oil meal	212·4			2·35	

* Average values for 20 chicks on each meal tested.

Table 16. *Protein quality and chemical characteristics of cottonseed meals from different mills* (CHANG *et al.*, 1955)

Mill designation	*No. of samples*	*Chick growth rate index*	*Total gossypol* (%)	*Nitrogen solubility in* 0·2N NaOH (%)	*Chemical index*	*Gossypol content of cottonseed kernels** (%)
D	2	75·2	0·72	81·6	96·0	0·65
H	3	74·6	0·84	77·6	91·3	0·74
I	3	74·6	0·73	77·0	90·6	0·67
E	3	69·5	0·85	74·1	87·2	0·67
J	3	71·8	0·81	70·0	82·4	0·69
A	1	52·1	0·86	68·5	79·7	0·69
F	3	64·3	1·05	69·2	65·9	0·81
B	3	59·9	1·06	67·9	64·1	0·91
C	2	54·6	1·02	65·8	64·5	0·76
G	3	51·8	1·23	68·8	55·9	1·01

* Rolled cottonseed meats used in the preparation of the meals.

nitrogen solubility are shown in Fig. 1 and Fig. 2, respectively. The correlation between the chick growth rate index and nitrogen solubility is not perfect, but it is good enough to be able to evaluate mill performance in the production of superior quality cottonseed meal. It will be noted that the chick growth rate index was never high when the meals contained more than 1·0 per cent of total

gossypol. Since all of these meals were low in free gossypol, total gossypol here is essentially bound gossypol. The meals used in the collaborative tests described above were produced in commercial mills under varied but carefully controlled conditions. They were manufactured during a study of pre-press-solvent mill operation by PONS *et al.* (1955). The effects of processing conditions on the physical and chemical properties of the meals have been described by these authors.

In order to obtain further information concerning the nutritional significance of bound gossypol BALIGA and LYMAN (1957) devised a procedure for the removal

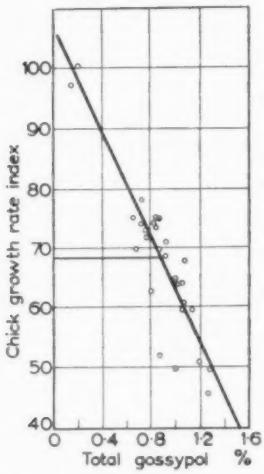

Fig. 1. The relationship of total gossypol to protein quality in cottonseed meal. (CHANG *et al.*, 1955)

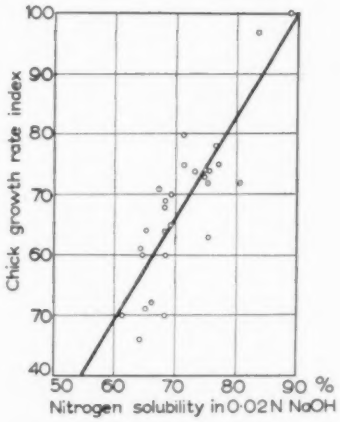

Fig. 2. The relationship of nitrogen solubility in 0·02N NaOH to protein quality in cottonseed meal. (CHANG *et al.*, 1955)

of most of the gossypol from a meal with low protein quality without the application of heat or other drastic treatment. Table 17 shows the results of the nutritional tests on this meal. Marked improvement was shown in protein quality as measured by the rat protein repletion test of Cannon, by the chick growth test and by the determination of lysine availability. Protein solubility was also improved. The conclusion to be drawn is that the low nutritive value of this original meal was not due primarily to heat damage to the protein but rather to the formation of a gossypol–protein compound which could not be digested properly.

The practical problem of producing superior cottonseed meals for hogs and poultry is difficult because the content of free gossypol must be reduced to fairly low levels, and if this is done by moist heat treatment then the gossypol combines with the protein and the result is low protein quality. The answer is either to remove the gossypol completely or to combine it in some way which leaves the protein free. The pre-press-solvent process offers one means of manufacturing superior-quality meals because in a typical operation considerable

Table 17. *Effect of removing bound gossypol on the nutritional value of cottonseed meal protein* (BALIGA and LYMAN, 1957)

Group no.	*Meal description*	*Gossypol content*		*Nitrogen solubility in* 0·02N NaOH (%)	*Lysine availability* (%)	*Rat protein repletion value, wt. increase in* 10 *days* (g)	*Chick growth av. gain for* 4 *week* (g)
		Free (%)	*Bound* (%)				
1	Original meal	0·033	1·32	61·0	54·9	26·0	121·7
2	Treated to remove free gossypol	0·003	1·10	69·0	54·1	29·0	157·8
3	Treated to remove bound gossypol	0·004	0·49*	77·0	70·4	46·0	222·4
4	Standard (Butanone extracted)	0·006	0·37	89·0	87·5	55·0	233·2

* Includes 0·42 per cent dianilino gossypol.

gossypol goes into the oil to be removed later during refining. In another commercial process the gossypol is combined by an aromatic amine, thus leaving the protein free.

It is to be expected that premium-quality meals could be manufactured more easily from seed which is low in gossypol. PONS *et al.* (1953) have evaluated eight strains of cotton for differences in gossypol level. A condensed summary of their data is given in Table 18.

Table 18. *Gossypol in moisture free cottonseed kernels of eight varieties expressed as a percentage of moisture free kernals* (*data from* PONS *et al.*, 1953)

Variety	1947	1948	1949	*Mean*
Acala 4–42	0·75	0·82	0·94	0·84
Acala 1517W	1·06	1·09	1·27	1·14
Rowden 41B	1·21	1·30	1·44	1·32
Mebane	1·09	1·10	1·25	1·15
Stoneville 2B	1·11	1·16	1·32	1·20
Deltapine 15	1·08	1·18	1·36	1·21
Coker 100W	1·11	1·21	1·34	1·22
Coker Wilds	0·89	0·99	1·16	1·01
Mean	1·04	1·11	1·26	1·14

As the problem stands today extensive new markets have been established for premium quality cottonseed meal to be used in feeds for poultry and swine.

At the Third Conference on Processing as Related to Nutritive Value of

Cottonseed Meal which was held in New Orleans, La., Nov. 9–11, 1953, the following recommendations were approved by the group composed of representatives from a number of State Agricultural Experiment Stations, from several branches of the U.S. Department of Agriculture, and from industry.

Statement of Policy Regarding Use of Cottonseed Meal in Feedstuffs

A. Results presented thus far indicate that chick and broiler rations containing cottonseed meal and soybean meal in equal proportions on a nitrogen basis are equal or superior to rations based on either cottonseed meal or soybean alone, when the cottonseed meal used has 0·04% or less of free gossypol and 75% or more of nitrogen solubility in 0·02N NaOH solution.
Nutrition investigators representing industrial, federal, and state organizations are invited to conduct experiments based on this statement using cottonseed meal of known processing history and chemical characteristics and soybean meal of high quality.

B. Preliminary indications are, insofar as free gossypol is concerned, that cottonseed meals having 0·04% or less of free gossypol can be fed in unrestricted proportion in balanced diets for chicks, broilers and swine.

To date, these recommendations have seemed to work out very well. Some mills have had difficulty in maintaining nitrogen solubility as high as specified in the recommendations.

Attempts to produce cottonseed meal which will not cause discoloration of eggs held in cold storage have not been as successful as the efforts to produce meal for use in feeds for growing chicks and pigs. The quantities of free gossypol which will cause egg discoloration are extremely small. As a consequence, cottonseed meal is still not recommended for laying hens. An important fundamental contribution toward an understanding of egg discoloration has been the recent report of Grau *et al.* (1954) who showed that gossypol in the diet of hens results in the accumulation in the eggs of a gossypol compound which appears to be gossypol cephalin. A quantitative procedure for measuring this substance in eggs was described. It is anticipated that the test will prove to be a valuable tool in the development of new methods for processing cottonseed meal.

IV. The Significance of Fat in Oilseed Meals

With an ever-increasing adoption of modern processing methods for the production of vegetable oil and meals, more and more meal is being placed on the market with low oil content. This efficiency in extraction is an accomplishment of which the industry as a whole can certainly be proud. At the same time, it is well to evaluate the practical significance of lowered oil content in the meal in terms of the value of the meal for use in farm rations. As a starting point for our discussion some of the most important functions of fat in farm feeds may be listed. They are as follows:

(*a*) Source of essential fatty acids
(*b*) Source of energy
(*c*) Improved digestion and absorption of other nutrients
(*d*) Improved palatability
(*e*) Improved physical characteristics of feed

The problem then is to evaluate the significance of a change of fat content of oilseed meals in terms of each of these functions.

The important fact to be considered in connection with the first function of fat listed above is that very small amounts of unsaturated fatty acids, those with two or more double bonds, are required by rats and certain other species. In the complete absence of these essential fatty acids the rats fail to grow, the skin becomes rough and unhealthy, necrosis of the tail frequently occurs and the animals finally die. A requirement for essential fatty acids by chicks has been demonstrated by REISER (1950), and it is not improbable that any farm animal would die if completely deprived of these essential fatty acids. The important consideration is that grains, hay and practically any natural farm feed has sufficient amounts of this type of fatty acid, and a deficiency never occurs in practical diets, but only in synthetic diets completely devoid of fat. There is, therefore, no disadvantage in reducing the fat content of cottonseed meal on the basis of the first function of fat listed above.

In considering energy derived from fats, some well-established and well-known principles should be kept in mind. First, all farm animals can effectively convert carbohydrates to fat for storage and use in their bodies. Second, small amounts of preformed fat in the diet can unquestionably be digested and effectively utilized by the animals. Third, the energy content of a pound of fat is 2·25 times greater than that of a pound of carbohydrate.

Now let us look at two sacks of oilseed meal both of equal protein content, of which one contains 6 per cent fat and the other 1 per cent fat. In the second case 5 lb of fat have been extracted by solvent extraction and the difference made up with 5 lb of hulls. Now this difference of 5 lb of fat is equivalent to 11·25 lb of digestable carbohydrates. Actually, the conversion of carbohydrate to fat is never quite 100 per cent efficient, and so in reality we would need a little more than 11·25 lb of carbohydrate to make up the difference between the two sacks of meal.

This difference in actual nutritive value is certainly there, but its practical significance may well be over emphasized. Suppose, for example, that we have cattle on a range with an abundance of dried grass which can supply the carbohydrate or energy needs of the animals. We are then buying cottonseed meal primarily because we need protein. In such a case a change in fat content of the cottonseed meal may be of very little importance.

There is abundant experimental evidence which shows that fat in the diet facilitates the utilization of certain other nutrients, among these may be mentioned the fat-soluble vitamins and possibly calcium. From a practical standpoint perhaps, the effect on the absorption of carotene is of greatest importance. Generally, the experimental feeding trials which demonstrate this beneficial effect of fat (MUELDER and KELLY, 1942) have been with rations varying substantially in fat content, e.g. from 2·5 per cent fat to 6·5 per cent fat. Now let us see what is the change in total fat content of a ration when we substitute an oilseed meal of 1 per cent fat for an oilseed meal containing 6 per cent fat. The differential in the meal itself is 5 per cent, but if we are feeding a ration which

contains only 10 per cent meal then the differential in the total diet is only 0·5 per cent. It is questionable whether a differential of this magnitude can ever cause measurable differences in carotene utilization. A sample calculation showing the fat differential in a beef cattle ration with solvent and hydraulic cottonseed meal is given in Table 19.

Table 19. *The effect of the fat content of cottonseed meal on the total fat content of a beef cattle ration*

Daily ration	*Fat contributed to ration*	
	Ration No. 1	*Ration No.* 2
	%	%
10 lb corn, 3·6% fat	1·26	1·26
16 lb hay, 2·4% fat	1·35	1·35
2·5 lb cottonseed meal, 6% fat	0·53	—
or 0·5% fat	—	0·04
Total fat content of ration	3·14	2·65

In special cases where oil seed meal is fed with rations of unusually low fat content, such as for example cottonseed hulls with only a bare minimum of green hay necessary to supply the necessary carotene, the significance of changes in the fat content of the meal may be somewhat greater than would be anticipated from the sample calculation given above.

The relationship between the oil content of oilseed meals and the palatability of the products for farm animals is very difficult to measure quantitatively. There are perhaps a few statements on which all would agree. The first is that if a diet for hogs or chickens is dusty, if it gets into the animals' nostrils, if it gums up in their mouths, or if for any other reason they do not like it, the food consumption will be below normal and the results will not be good. The second fact is that small amounts of oil in a ration do reduce dustiness and hence are of some value of this reason.

Dry powdery meals are more difficult to handle in windy weather, they are more difficult to pellet, losses of material due to sifting through bags are greater and it is more difficult to maintain such meals as homogenous mixtures in mixed feeds. There is no question but that fat improves these qualities.

When we compare high and low fat cottonseed meals in actual feeding trials, the results should reflect a summation of the factors listed above in so far as they apply to the particular type of feeding operation used in the test. Some general conclusions formulated from the results of the work of numerous investigators are given below.

A. Beef cattle

A summary of twenty-two feeding trials comparing hydraulic and solvent extracted cottonseed meals has been prepared by the Educational Service of the

National Cottonseed Products Association. In view of the fundamental considerations discussed above, it is not surprising to find that the unweighted averages for the two types of meal were essentially the same. The average daily gain on solvent extracted meal was 1·65 lb and for the hydraulic meal 1·67 lb. This would indicate that the two types of meal are very nearly equal *as protein supplements* for cattle.

B. Dairy cattle

At the New York Agricultural Experiment Station at Cornell seventeen different experiments (1932–1945) were conducted to determine the difference in production with dairy rations containing 2·7 per cent fat as compared to rations containing about 6·5 per cent fat. On an average the higher fat rations gave a 4 per cent increase of milk. It must be kept in mind that the fat differential between these two types of rations was about 4 per cent and that the fat differential which would result from replacing hydraulic cottonseed meal with solvent-extracted meal would be more likely about 0·5 per cent for the total ration. It is well to remember that it has been definitely shown that good milk production (probably not quite maximum) can be obtained with rations containing only 2·5 per cent fat.

C. Swine

In both growth and reproduction tests it has been shown that swine do well on rations containing as little as 0·5 per cent fat (Ellis and Zeller, 1930). On such rations the feed required to produce a pound of gain is greater. Considering the fat content of all of our common grains, it is evident that any practical ration for swine would contain considerably more than 0·5 per cent fat.

D. Poultry

At the New Jersey Station it was found that rations containing only 0·1 per cent fat gave almost as good results as a normal ration (Russell *et al.*, 1940).

During experiments at the Texas Station on the development of a method for protein quality evaluation in cottonseed meal (Lyman *et al.*, 1953) by chick feeding tests, tests were also carried out to determine the effect of small amount of fat in chick rations. In these tests cottonseed meal supplied the only source of protein and the energy source was cerelose, (a fat-free carbohydrate preparation). Table 20 shows the growth rate data obtained on the rations without added cottonseed oil as compared to simultaneous tests where the total content of fat was adjusted to 4 per cent by the addition of cottonseed oil. It will be seen that the differences in rate of gain are very small.

As we look at the whole picture concerning the question of the fat content of oilseed meals the most important factor appears to be the question of the physical properties of the products. Solvent extracted meals are difficult to pellet and when they are pelleted the product is likely to be too hard. Special machines have been designed for cottonseed pelleting but this is not the most desirable solution for the industry as a whole.

Within the last few years it has been found that the addition of one to two

per cent of acidulated soap stock to solvent extracted meals solves the pelleting problem, and also the problem of dustiness in loose meal. Several factors make this a very satisfactory answer to the problem. By this procedure the nutritional value of fatty acids is added back to the meal. At the present time the price of soap stock is low enough to justify this use. The conversion of the basic soap

Table 20. *The effect of the fat content of the diet on the rate of gain of chicks*

Protein source	*Fat content of diet* (%)	*4 week gain* (g)	*Fat content of diet* (%)	*4 week gain* (g)
S. O. M. 1·5% fat	0·7	264	4·0	267
C. S. M.–S–6–76 0·2% fat	0·1	272	4·0	282
Solvent C. S. M.				
Sample A, 2·0% fat	1·0	277	4·0	298
Sample B, 1·8% fat	0·9	274	4·0	306
Sample C, 1·6% fat	0·8	345	4·0	330

stock to free fatty acids is a relatively simple procedure and many companies owning oil mills also have soap stock to sell.

Although cottonseed foots contain rather large amounts of gossypol decomposition products, feeding trials with chicks have demonstrated that the small amounts in the diet from this source do not result in growth retardation.

Perhaps a word of warning is desirable. Acidulated soap stock to be added back to feeds must be protected from becoming rancid because rancidity in farm feeds is always detrimental to the animals. Where the products are to be stored for some time before being added back to the meal, a suitable antioxidant is highly desirable if not essential.

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5

THE COMPOSITION AND PROPERTIES OF FISH OILS

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5

THE COMPOSITION AND PROPERTIES OF FISH OILS

L. A. Swain

I. Occurrence

Tremendous quantities of fat are produced in the world, amounting to over 26 million metric tons in 1952. Of this quantity only 3 per cent was listed as from marine sources. (Duncan, 1953). This fish oil is obtained throughout the world, as shown in Table 1 (for 1951), with Norway and the United States as major sources. Iceland and Canada are next in importance as sources, and the United Kingdom and South Africa follow them. Fig. 1 shows how little of the area of the oceans is as yet utilized. Explorations in more distant waters are now progressing.

Table 1. *Fish oil production (metric tons) in certain countries in* 1951. (*From Table* 10, 1950–51 Yearbook of Food and Agricultural Statistics)

Source	*Cod liver*	*Herring and other Clupeidæ*	*Shark liver*	*Others*	*Total*	*% of total*
West Pacific						
Japan	1,000	3,000	—	—	4,000	1·6
North America						
Canada	5,135	15,624	300	1,176	22,235	8·6
Unites States	590	54,613	340	6,296	61,839	24·0
East Atlantic						
Iceland	7,500	10,844	—	5,155	23,499	9·1
Norway	15,800	80,000	1,400	340	97,540	37·9
Denmark	—	4,000	—	1,000	5,000	1·9
U. K.	14,809	2,459	—	—	17,268	6·7
Ireland	—	—	381	—	381	0·1
France	2,454	—	—	—	2,454	1·0
Belgium	93	24	—	—	117	—
Netherlands	—	—	—	4,400	4,400	1·7
Portugal	—	—	—	3,076	3,076	1·2
S. Africa	—	15,260	—	—	15,260	5·9
Total	47,000	186,000	2,000	21,000	257,000	

Fig. 1 shows also the areas of the world where a given species tends to congregate, insofar as is known. This distribution is given in greater detail in Table 2, which shows the continent near which fish are caught. Here it is estimated that over 10 per cent of the fish caught in the world is reduced to oil and

Table 2. World catch of fish by species (millions of metric tons) and percentage converted to oil (estimated by FAO for mid-twentieth century)
(*From Table* 1, 1950–51 Yearbook of Food and Agricultural Statistics)

Species	*North America*	*South America*	*Europe*	*Africa*	*Asia*	*U.S.S.R.*	*Total*
Teleost fresh- and brackish-water spp.	0·1	0·1	0·1	0·1	3·5	0·7	4·6
Salmon, trout, etc.	0·3	—	—	—	0·1	0·2	0·6
Teleost flat fishes	0·1	—	0·2	—	0·2	0·1	0·6
Cod, hake, haddock and sim. spp.	0·6	—	2·2	0·1	0·3	0·2	3·4
Herring, sardines, pilchards, and sim. spp.	1·3	—	2·1	0·4	2·0	0·6	6·4
Tuna, mackerel and sim. spp.	0·3	0·2	0·2	—	0·7	—	1·5
Other marine teleosts	0·4	0·2	0·8	0·1	3·0	0·4	5·0
Elasmobranchs	—	—	0·1	—	0·2	—	0·5
Total	3·8	0·5	6·0	0·9	12·0	2·5	25·9
Wt. reduced to oil and meal	0·8	—	1·2	0·3	0·4	—	2·7
as % of geographical area catch	21	—	20	33	3·3	—	
as % of world catch	3·1	—	4·6	1·2	1·5	—	10·4

meal, that almost half of that quantity is reduced in Europe, and that almost one third is reduced in North America.

It would seem self-evident that only the oilier fishes will be reduced in quantity to obtain the oil from them. Hence Europe, which catches the greatest quantity of the fatty *Clupeidæ* of any area in the world, will be a major producer of the oil from this source. But in Asia, where almost as much of these species is caught, fish probably enter directly into the edible market and oil is therefore not prepared commercially. China and India, for example, import fish oils but export none (Food and Agricultural Organization, 1953). From the data in Table 3 (calculated from the above publication) one may see which species are important producers of oil.

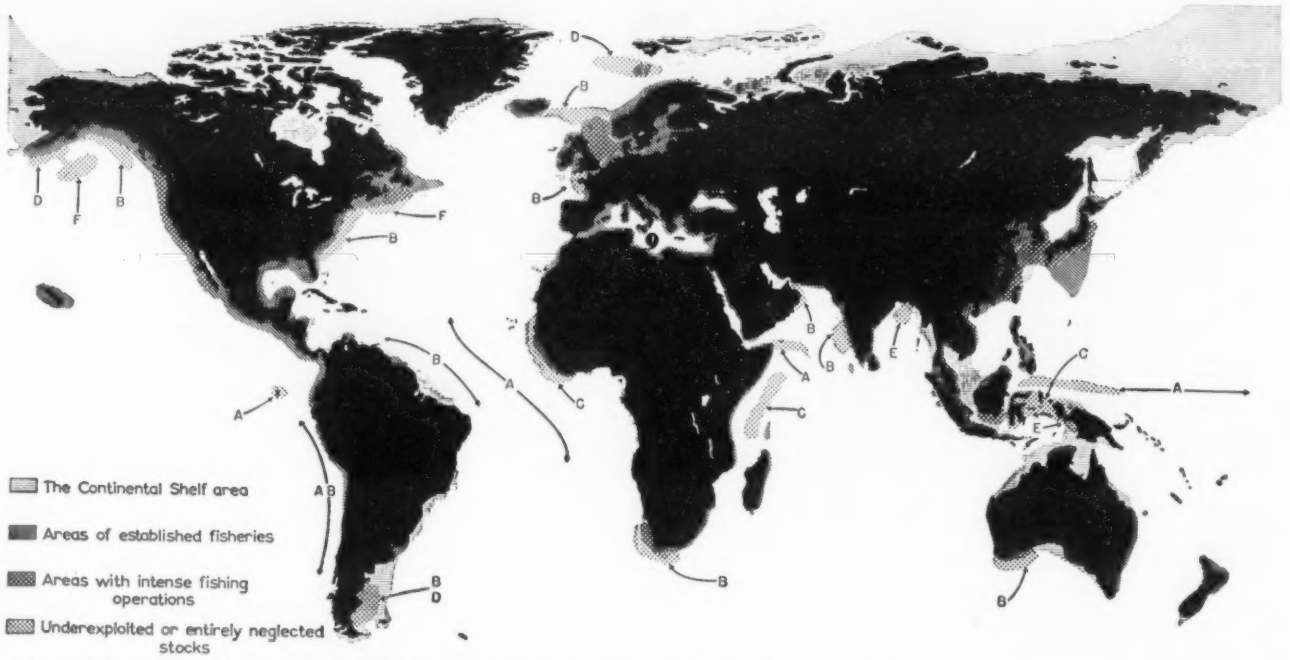

The Continental Shelf area
Areas of established fisheries
Areas with intense fishing operations
Underexploited or entirely neglected stocks

Fig. 1. Marine fisheries of the world, showing areas of established fisheries, those intensely exploited, and those under-exploited or entirely neglected. After United Nations Department of Economic Affairs, *Proceedings of the United Nations Scientific Conference on the Conservation and Utilization of Resources*, Vol. 7. *Wildlife and Fish Resources*, New York, 1951. A—tuna; B—Clupeoid; C—Percomorph, as reef stocks; D—Gadoid; E—Crustacea; F—redfish.

Table 3. Fish reduced to oil and meal in 1951 by certain species and countries.
(*From Table 5, 1950–51 Yearbook of Food and Agricultural Statistics*)

Country	*Fish*	*Metric tons*	*% of total production of that fish*
Canada	Herring	155,803	57·3
Newfoundland	Salmon, etc.	4,355	21·7
	Herring, etc.	8,358	29·3
United States	Cod, hake, etc.	22,700	11·6
	Herring	538,900	72·8
Chile	Cod, hake, etc.	21,146	49·4
	Herring, etc.	5,492	64·1
Japan	Flatfish	27,604	27·8
	Cod, hake, etc.	118,354	56·1
	Herring, etc.	62,621	7·3
	Perches, etc.	5,599	2·4
	Elasmobranchs	28,808	33·6
Denmark	Other marine teleosts	88,200	72·2
Finland	Herring, etc.	3,600	12·0
Iceland	Herring, etc.	59,466	70·3
	Perches, etc.	65,464	64·2
Netherlands	Fresh water teleosts	8,975	55·3
	Herring, etc.	14,250	2·1
	Tuna, etc.	1,300	12·3
	Jacks, pompanos, etc.	225	100·0
	Other marine teleosts	1,225	85·9
	Elasmobranchs	52,000	78·6
United Kingdom	Herring, etc.	23,505	13·3
	Tuna, etc.	2,174	34·4

The portion of the fish from which oils can be extracted in quantity varies with the species. In some the liver contains a very large proportion, for example:

		% oil
Pacific dogfish	*Squalus suckleyi*	40–70
Atlantic dogfish	*Squalus acanthias*	13–75
Pacific basking shark	*Cetorhinus maximus*	60–80
Pacific gray cod	*Gadus macrocephalus*	12–45
Atlantic hake	*Urophycis* sp.	33–55
Atlantic cod	*Gadus morrhua*	20–70

In others the flesh is very oily:

Atlantic menhaden	*Brevoortia tyrannus*	5–20
Atlantic shad	*Alosa sapidissima*	10–20
Pacific spring salmon	*Oncorhynchus tshawytscha*	13
Pacific pilchard	*Sardinops caerulea*	5–25
Pacific herring	*Clupea pallasii*	5–25

In some there is oil in the viscera (abdominal contents less liver). This source was of importance in the heyday of the fish-oil vitamin industry, for this oil contained considerable vitamin A. Little, if any, is now prepared separately.

The distribution of oil in the South African pilchard is shown in Table 4. The oil content of organs and tissues of many other South African fishes is given in Table 14.

Table 4. Distribution of oil in South African pilchard. (*From* BLACK and SCHWARTZ, 1950)

Source of oil	*October*	*May*
Oil in whole fish (%)	3·7	14·2
Oil in head (% of head)	6·7	10·1
Oil in body (% of body)	3·3	14·0
Oil in liver (% of liver)	4·0	5·1
Oil in other viscera (% of other viscera)	1·7	22·1
Oil in head (% of total oil)	30·3	12·8
Oil in body (% of total oil)	61·7	66·9
Oil in liver (% of total oil)	2·7	0·4
Oil in other viscera (% of total oil)	5·2	12·8

II. COMPOSITION

A. Unsaponifiable matter

Fish oil, like any fat, is predominantly glyceride in composition. Dissolved in these glycerides is a number of compounds, most of which are the source of the unsaponifiable matter (unsap) of the oil. They are frequently much higher in concentration in fish oils than they are in land oils and fats. The unsaponifiable matter of an oil is that portion of the saponified oil which is soluble in an organic solvent immiscible with water. Each is a mixture of many compounds; examples are shown in Tables 5 to 14. The amount present shows great variations as

Table 5. Composition of unsap from liver oil of various sharks. (*From* KARNOVSKY *et al.*, 1948a,b,c)

Liver oil from	*% unsap*	*Composition*
Basking shark (*Cetorhinus maximus*)	30–50	Mainly squalene and pristane
Spiny shark (*Echinorhinus spinosus*)	50	Squalene and some glyceryl ethers
Seven-gilled shark (*Heptranchias pectorosus*)	20	Glyceryl ethers
Soupfin shark (*Galeorhinus canis*)	10	Vit. A, sterols, glyceryl ethers and fatty alcohols.

may be seen in subsequent tables. This unsap may contain two types of compounds. Hydrocarbons form a major portion of the unsap of a few oils, for example, the liver oil of the basking shark (*Cetorhinus maximus*) in which these compounds may comprise half of the oil, and form a minor portion of many others. Alcohols form the balance of the unsap. They may occur naturally in the free form but are normally esterified. These alcohols include very important components of the oil—such things as vitamins and pigments.

Table 6. Composition (% by wt.) of soupfin shark-liver oil unsap (1·99% of oil). (*From* KARNOVSKY *et al.*, 1948a)

Vitamin A	11·2	Squalene	3·8
Cholesterol	28·7	Sat. hydrocarbon	2·2
α-glyceryl ethers (as selachyl alc.)	21·7	Fatty alcs. (as oleyl)	29·0

Table 7. Composition (% by wt.) of unsap from pilchard and maasbanker oils. (*From* BLACK and SCHWARTZ, 1950)

	Pilchard oil unsap	*Maasbanker oil unsap*
% unsap	6·4–1·6	2·26
Cholesterol	67·0–63·8	49·4
Glyceryl ethers	3·6–8·6	8·0
Squalene	1·7–2·8	2·3
Satd. hydrocarbons	5·1–18·9	12·4
Fatty alc. (docosenol?)	10·3–17·9	21·4

Table 8. Composition of unsap of oil from various organs of basking shark. (KARNOVSKY and RAPSON, 1947)

Oil from	*Oil yield* (%)	*Unsap* (%)	*% of oil*			
			Squalene	*Satd. hydroc.*	*Glyceryl ethers*	*Sterols*
Liver	70	47·7	39·5	6·4	0·4	0·2
Flesh (tail)	10·1	21·4	0·8	—	20·6	0·6
Spleen	0·5	59·6	3·6	—	5·1	48·4
Kidney	0·8	45·9	1·8	—	1·3	40·9
Epididymis	0·5	53·3	1·2	—	3·0	47·4
Eye-socket	0·05	30·7	4·2	—	—	—
Gristle (under skin)	—	21·1	0·5	—	—	—

A means for the fractionation of fish oil unsap by a chromatographic method was described by SWAIN (1948). Elution of an unsap adsorbed in a column of activated alumina by different solvents in succession yielded fractions of the following composition:

light petroleum —hydrocarbons
methylene chloride—primary alcohols (cholesterol, vitamin A, pigments)
ethyl ether —glyceryl ethers
methanol —balance, composition undetermined

Results obtained by this method are given in Table 9.

Table 9. Composition of unsap of several eastern Pacific fish liver oils. (SWAIN, 1948)

Unsap from liver oil of	*% eluted by*			
	Light petroleum (hydrocarbons)	*Methylene chloride (primary alcohols)*	*Ethyl ether (glyceryl ethers)*	*Methanol (?)*
Halibut (*Hippoglossus stenolepis*)	1·0	91·8*	9·3	4·9
Lingcod (*Ophiodon elongatus*)	1·7	78·6†	12·3	6·5
	1·6	78·7†	12·2	5·1
	1·3	70·0	18·8	5·7
	1·7	69·1	17·7	7·5
Basking shark (*Cetorhinus maximus*)	98·1	5·4	1·3	1·6
Soupfin shark (*Galeorhinus galeus*)	2·8	40·8	11·9	36·3
Mackerel shark (*Isurus nasus*)	1·7	77·7	4·9	12·1
Ratfish (*Hydrolagus colliei*)	1·2	29·7	68·6	1·7

* Benzene
† 2 per cent ether in benzene

Table 10. Hydrocarbons reported in fish liver oils. (*After* BAILEY *et al.*, 1952)

Name	*Formula*	*No. of double bonds*	*Occurrence*
Decane	$C_{10}H_{22}$	0	Shark
Pristane	$C_{19}H_{38}$	0	Shark
Zamene	$C_{18}H_{36}$	1	Basking shark
Gadusene	$C_{18}H_{32}$	3	Cod
Cetorhinene	$C_{28}H_{46}$	6	Basking shark
Squalene	$C_{30}H_{50}$	6	Various fishes

Hydrocarbons were first discovered in fish oils by TSUJIMOTO (1906) who isolated some from ai-zamé (*Centrophorus* spp.) and from Kurokozami (*Zameus* spp.). Ten years later he proposed the name 'squalene' for this hydrocarbon (TSUJIMOTO, 1916). Just before this time a fish oil shipped from Lisbon to London was found to contain 83 per cent unsap, most of which was hydrocarbon, and the oil was condemned because of claimed adulteration. It was later shown that certain authentic Mediterranean fish liver oils did contain such large proportions of unsap (MASTBAUM, 1915). Japanese workers have continued to isolate hydrocarbons from fish oils, and similar compounds have been found in fish oils in other parts of the world. Results of these efforts are summarized in Table 10.

Table 11. *Squalene in South African fish oils.*
(*From* KARNOVSKY and RAPSON, 1947)

Common name	*Scientific name*	*Oil from*	*% unsap in oil*	*Unsatd. hydroc. in oil calc. as % squalene*
Seven-gilled shark	*Heptranchias pectorosus*	liver	19·6	0·2
Six-gilled shark	*Hexanchus griseus*	liver	22·8	0·3
Angler fish	*Lophius piscatorius*	liver	2·6	0·1
Kabeljaauw	*Sciaena hololepidota*	liver	8·7	0·4
Soupfin shark	*Galeorhinus canis*	liver	2·7	0·05
Man-eater	*Carcharodon carcharias*	liver	36·1	33·6
Basking shark	*Cetorhinus maximus*	liver	47·7	39·3
Basking shark	*Cetorhinus maximus*	kidney	45·9	1·9
Spiny shark	*Echinorhinus spinosus*	liver	49·9	43·6
Deepsea dogfish	*Centroscymnus fuscus*	liver	91·5	90·4
Cacao	*Centroscymnus* sp.	liver	94·1	95·2
Common chimaera	*Chimaera monstrosa*	liver	74·8	62·8

Table 12. *Cholesterol content of several fish liver oils.*
(*After* PIHL, 1952)

Fish	%	*Fish*	%
Atlantic dogfish	3·7	Coalfish	0·35
Atlantic herring	0·38–0·90	Basking shark	0·4
Cod	0·57	Pacific halibut*	7·7

* KRISTJANSON (1951).

Table 13. *Composition of α-glyceryl ether fraction* (89·2%) *of unsap of oil from liver of seven-gilled shark* (*Heptranchias pectorosus*). (*From* KARNOVSKY *et al.*, 1948b)

Length of sidechain, C	*Saturated* (%)	*Mono-unsaturated* (%)	*Di-unsaturated* (%)
16	13·0	18·1	
18	16·2	42·3	
20		6·8	
22			2·9
24			0·8

The content of unsaturated hydrocarbons in South African fish oils, calculated as squalene, is given in Table 11 (KARNOVSKY and RAPSON, 1947). The hydrocarbon content of a number of eastern Pacific fish-liver oils is given in Table 9 (SWAIN, 1948). A further survey of squalene occurrence is given by FITELSON (1943).

Table 14. *Occurrence of α-glyceryl ethers in fish.*
(*From* KARNOVSKY *et al.*, 1946)

Common name	*Scientific name*	*Oil from*	*% unsap in oil*	*Glyceryl ethers in unsap, as % selachyl alcohol*	*Glyceryl ether esters in oil, as % selachyl dioleate*
Seven-gilled shark	*Heptranchias pectorosus*	1. liver	22·39	94·3	53·7
Seven-gilled shark	*Heptranchias pectorosus*	2. liver	19·55	89·2	44·4
		intestine	59·12	3·0	4·5
		flesh (0·4%)	12·43	20·6	6·5
		3. liver (40·4%)	26·11	88·7	58·9
Six-gilled shark	*Hexanchus griseus*	1. liver (60%)	22·82	77·7	45·1
Six-gilled shark	*Hexanchus griseus*	2. liver	32·10	92·7	77·5
Walbeehm's sharp-nosed shark	*Carcharinus walbeehmi*	liver	3·68	20·5	1·9
Lazy grey shark	*Carcharinus melanopterus*	liver	35·60	6·1	5·5
Dusky shark	*Carcharinus obscurus*	1. liver	5·43	9·4	1·3
		2. liver (58%)	7·95	0·8	0·2
Blue shark	*Carcharinus glaucus*	liver	8·72	32·5	7·2
Blackfin shark	*Carcharinus limbatus*	liver	3·10	21·2	1·7
Tiger shark	*Galeocerdo arcticus*	1. liver	1·85	17·7	0·8
		2. liver	3·00	34·4	2·6
		3. liver	1·87	24·2	1·2
		embryo liver (44·3%)	8·82	0·4	0·1
		yolk sacs (14·0%)	10·30	2·1	0·6
Smooth hound	*Mustelus laevis*	1. liver (46%)	5·12	22·83	3·0
		2. liver (46%)	4·93	22.5	2·8
Common hound	*Mustelus canis*	liver	2·71	28·5	2·0
Hammerhead shark	*Sphyrna zygaena*	liver	4·10	0	0
Blue pointer shark	*Isurus glauca*	liver (6·5%)	4·32	18·7	2·1
Man-eating shark	*Carcharodon carcharias*	liver	36·13	0	0
Basking shark	*Cetorhinus maximus*	1. liver (70%)	47·73	0·9	1·1
		flesh (10·1%)	21·39	96·2	52·4
		kidney (0·8%)	45·90	2·8	3·3
		spleen (0·52%	59·58	8·5	12·9
		epididymis (0·52%)	53·36	5·6	7·6
		2. liver	32·75	1·6	1·3
		3. liver (78%)	35·32	2·3	2·0
		flesh (5·4%)	19·25	60·0	28·9

Table 14—continued

Common name	*Scientific name*	*Oil from*	*% unsap in oil*	*Glyceryl ethers in unsap, as % selachyl alcohol*	*Glyceryl ether esters in oil, as % selachyl dioleate*
Slender-toothed shark	*Carcharias taurus*	liver	2·41	16·9	1·0
Cape dogfish	*Scylliorhinus capensis*	liver (23·2%)	2·56	14·9	1·0
Striped dogfish	*Scylliorhinus africanus*	liver (42·3%)	2·98	9·5	0·7
Variegated dogfish	*Scylliorhinus pantherimus*	1. liver (46%)	2·95	13·3	1·0
		2. liver (43·8%)	2·43	16·6	1·0
Spiny shark	*Echinorhinus spinosus*	1. liver (70%)	45·95	10·7	12·5
		2. liver	49·70	9·5	12·0
Dogfish	*Squalus* sp.	liver	27·40	77·3	53·9
Deepsea dogfish	*Centroscymuus fuscus*	1. liver (71·5%)	91·50	1·5	3·6
		2. liver (60·0%)	86·70	2·6	5·7
	Centroscymuus sp.	liver (90%)	94·10	1·2	2·8
		flesh (0·4%)	22·33	2·2	1·2
Sand shark	*Rhinobatus* sp.	liver	3·58	24·73	2·3
Common chimaera	*Chimaera monstrosa*	liver (58%)	74·80	14·5	27·6
Cape Joseph	*Callorhynchus capensis*	liver (50·0%)	2·44	66·6	4·1
Sardine	*Sardina sagax*	1. whole fish	4·09	2·1	0·2
		2. whole fish	2·97	6·5	0·5
Cape eel	*Congermuraena australis*	liver (5·6%)	11·80	8·7	2·6
		body (2·9%)	6·96	4·2	<0·8
Haarder or mullet	*Mugil cephalus*	liver (7·2%)	5·79	1·3	0·2
		intestine (11·6%)	9·30	1·5	0·4
		head (19·3%)	2·85	0·4	0·1
Stockfish (hake)	*Merluccius capensis*	liver	3·55	15·5	1·4
Super sole	*Austroglossus microlepsis*	liver (9·9%)	9·52	9·3	2·3
		body (4·9%)	5·31	36·7	5·0
Stone bass	*Polyprion americanus*	liver (4·2%)	22·25	12·8	7·3
Yellowtail (albacore)	*Seriola lalandii*	liver	8·48	17·5	3·8
Kabeljaauw	*Sciaena hololepidota*	liver	8·70	2·7	0·6
	Sciaena hololepidota	head	3·26	11·3	0·9
Red stumpnose	*Pagrus gibbiceps*	liver	14·43	5·9	2·2
Rosefish	*Pagellus erythrinus*	liver (7·2%)	5·91	10·3	1·6
		body (4·1%)	2·95	12·5	0·9
		head (10·0%)	3·49	14·4	1·3

Table 14—*continued*

Common name	*Scientific name*	*Oil from*	*% unsap in oil*	*Glyceryl ethers in unsap, as % selachyl alcohol*	*Glyceryl ether esters in oil, as % selachyl dioleate*
'Fransch Madam'	*Boopsidea inornata*	total viscera (2·6%)	17·50	4·8	2·1
		body (3·8%)	3·76	10·8	1·0
		head (7·2%)	4·02	6·0	0·6
Red steenbras	*Dentex rupestris*	liver	51·20	1·6	2·0
Seventy-four	*Dentex undulosus*	liver	6·48	4·1	0·7
Blue hottentot	*Caranthus aeneus*	entire fish (4·0%)	3·81	0	0
Bamboo fish	*Box salpa*	entire fish (5·3%)	3·07	2·3	0·2
John Brown	*Gymnocrotaphus curvidens*	liver	—	1·7	—
		body (1·3%)	9·15	7·4	1·7
		head (9·1%)	3·20	21·0	1·7
Mackerel	*Scomber colias*	head	7·20	3·5	0·6
		body	9·40	1·4	0·3
Tunny	*Thunnus thynnus*	liver	40·34	3·5	3·6
Bonito	*Sarda sarda*	liver	7·61	4·8	0·9
		head	1·25	6·5	0·2
Toby or Blaasop	*Tetrodon* sp.	liver (23·6%)	3·31	13·0	1·1
Angler or monk-fish	*Lophius piscatorius*	liver	2·62	0·6	<0·1

The hydrocarbons mentioned above are colourless, but some hydrocarbons are pigmented. Of these only carotene has been reported in fish oils, and then only in small amounts.

The other components of the unsap of fish oils are very dissimilar among themselves in composition and in properties, but all possess one or more hydroxyl groups. They normally occur esterified with fatty acids, although varying proportions may occur in the free alcoholic form, depending upon the past history of the oil. These alcohols may be divided into groups, as follows: pigments, sterols, fatty alcohols, and glyceryl ethers.

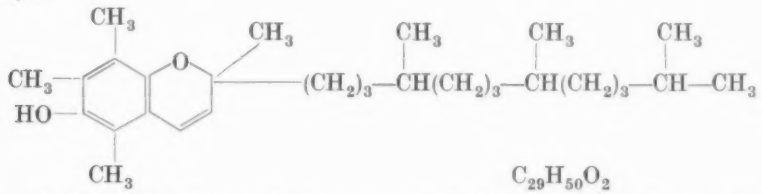
The pigments include xanthophylls such as zeaxanthin and taraxanthin in monk (angler) fish (Sorensen, 1934); fucoxanthin; astacin in brown trout (Steven, 1947), in angler fish liver oil (Burkhardt *et al.*, 1934), in salmon oil and *Cyclopterus lumpus* (Sorensen, 1935), and in Pacific salmon oils (*Oncorhynchus nerka* and *Salmo gairdneri*) in both of which two chromatographically different forms were present (Bailey, 1937). Astacin exhibits *keto–enol* isomerism and therefor› can not be extracted from an alkaline soap solution, in which it behaves as an acid. Under special circumstances it may separate as a third intermediate phase during unsap extraction.

In addition to these naturally occurring pigments there may be present others which have been introduced into the oil in various ways—either because of the conditions under which the fish had been stored, conditions under which the oil had been separated from the fish, or conditions under which the oil had been stored. The conditions which cause colour development are normally adverse. They are primarily high temperatures during processing, the need for which increases with decreasing quality of the original material, and contact with certain metals during processing and storage. Iron, lead and copper are notorious in this respect.

Sterols are present in all naturally occurring fats and oils; the particular ones present depend upon the source of the oil. All fish oils contain cholesterol, amounts varying with the species and also with the individuals within the species. The cholesterol content of several fish liver oils is shown in Table 12. WILBER and DEL PROMO (1949) have claimed that the lower content of cholesterol in arctic fish in comparison with non-arctic fish is correlated with the resistance of the fish to freezing injury.

The various D vitamins are sterols, varying one from another in minor details of molecular construction. Of these, vitamin D_3 is the one found in greatest proportion, although in some fish liver oils several are present. The presence of vitamin D in certain fish liver oils made these oils an important commodity until synthetic vitamin D became common.

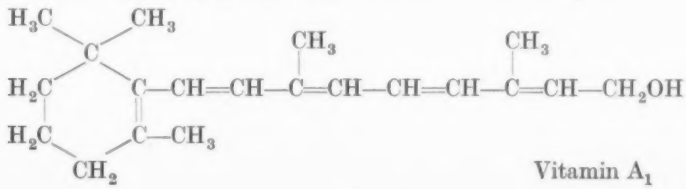
Vitamin E has been reported in small amounts in various oils from Brazil by ROBESON and BAXTER (1943) and in six species of fish caught around England (BROWN, 1953). Many compounds possess vitamin E activity, of which α-tocopherol is the most potent. The formula of α-tocopherol (MATTILL, 1952) is:



$C_{29}H_{50}O_2$

Simple fatty alcohols are of rare occurrence in fish oils, although several have been found in the ovary fat of the gray mullet (TSUJIMOTO, 1933), in the oil from the castor-oil fish (*Ruvettus pretiosus*) (COX and REID, 1932), and in certain shark liver oils (TSUJIMOTO, 1921). They are common in some whale oils.

The vitamins A may be considered as derived from simple fatty alcohols since they are alcohols possessing an ionone ring at the end of the molecule remote from the hydroxyl group. The formula of vitamin A_1 is:



Vitamin A_1

Recent work has shown that the vitamin A in fish livers may be any of several closely related compounds, having different biological activities. Vitamin A, like vitamin D, has been a major factor in the commercial development of the fish-liver oil industry. The development of synthetic vitamins A and D has struck this industry a major blow.

Glyceryl ether esters might be thought of as glycerides in which one terminal ester linkage is reduced to an ether linkage, being therefore of the form:

$$\begin{array}{l} CH_2OOC\ R' \\ | \\ CHOOC\ R'' \\ | \\ CH_2O\ R \end{array}$$

Saponification removes the two fatty acids, leaving glycerol connected to an alkyl group through an ether linkage at its α-carbon. Ethers vary in the size and unsaturation of this alkyl group. Although discovered originally in elasmobranch fishes by TSUJIMOTO and TOYAMA (1922), they have since been isolated in small amounts from various sources. The Japanese workers described three ethers—batyl in which R is C_{18}, chimyl in which R is C_{16}, and selachyl in which R is mono-unsaturated C_{18}. More recent work has shown the presence of more highly unsaturated ethers in fish oils (TOYAMA and TAKAHASI, 1939), has demonstrated that several compounds referred to as alcohols when originally reported were in reality these glyceryl ether alcohols (BERGMANN and STANSBURY, 1943; SCHULTZ and BECHER, 1933), and has demonstrated the presence of batyl alcohol in a land animal (HOLMES *et al.*, 1941). The variety of glyceryl ethers present in one oil is demonstrated in Table 13. The widespread occurrence of these ethers in South African fish oils is given in Table 14.

B. Fatty acid composition

A fish oil is primarily a mixture of glycerides. Like any other fat, then, it is made up of compounds consisting of glycerine completely esterified by fatty acids. These fatty acids are all alike in that almost without exception their molecules contain even numbers of carbon atoms. A terminal carbon is carboxyl, and some of the carbon atoms may be connected by double bonds. They vary among themselves in the length of the carbon atom chain, ranging from 4 carbons to as high as 26 (one containing 32 C atoms has been reported), and in the number of double bonds in the molecule, ranging from 0 to 6. Land forms of life generally contain fatty acids of carbon size 14 – 20 with 0 – 4 double bonds with smaller amounts of long chain—more highly unsaturated—acids. Marine forms contain larger proportions of longer carbon chain fatty acids of higher unsaturation. Approximately a third to a half of these fatty acids contain from 20 to 22 carbon atoms per molecule (in some fish oils as many as 26). All these molecular sizes of fatty acids, excepting possibly the shortest, contain fatty acids of varying degrees of unsaturation. The number of double bonds possible is a function of the size of the molecule. It is stated by LOVERN (1950) to be

generally as follows in marine forms, and these double bonds are fairly uniformly placed in the molecule:

C atom	No. of double bonds
16	1, or 3
18	1, or 4
20	1, or 4, or 5
22	1, or 5, or 6

The positions of the double bonds for a molecule of given length are not so uniform in marine oils as in land oils and the double bonds may more commonly be as frequent as 6 per molecule.

When the more soluble (more unsaturated) portion of the fatty acid methyl esters prepared from a fish oil is separated by crystallization and then molecularly distilled, the later distillates (highest temperature and therefore longest molecules) contain the most highly unsaturated esters. Here then is a readily accessible pool of material of very unusual occurrrence in land fats and oils, investigation of which may lead to new developments. Fatty acid composition of several fish oils is shown in Table 15 (DEUEL, 1951).

LOVERN (1942) described the variations that occur during a year in the composition of herring oil. The results are shown in Table 16. The herring do not feed during the winter but commence after April. The oil from April-caught fish is then most nearly typical of herring oil unaffected by feed. As feeding (mainly on *Calanus finmarchicus*) proceeds, the C_{18}, C_{20} and C_{22} acids become more unsaturated, a result to be expected from the composition of the food. But the C_{16} acids also become more unsaturated, the reverse of what might be expected from the composition of the food, and therefore a specific effect brought about by the herring. The October fish (non-feeding) then show a decrease in unsaturation of all these acids, approaching the April values.

Table 15. *Component acids* (% *by wt.*) *of body fats of some marine teleosts.* (DEUEL, 1951)

Genera and species	*Common name*	*Flesh fat* (%)	*Unsap in oil* (%)	*Saturated*			*Unsaturated*•					
				C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Clupea sprattus	Sprat	12	1	6·0	18·7	0·9	0·1	16·2	29·0 (3·0)	18·2 (5·5)	10·9 (7)	—
Sardinops caerulea	Pilchard	—	—	5·1	14·4	3·2	0·1 (2)	11·8 (2)	17·7 (3·3)	17·9 (4·1)	13·8 (8·5)	15·2 (10·9)
Clupanodon melanostica	Japanese sardine	10–18	0·5–1·5	6	10	2	—	13	24 (2)	26 (5)	19 (5)	—
Alosa menhaden	Menhaden-shad	10–16	0·6–1·6	6	16	1·5	—	15·5	30 (4)	19 (10)	12 (10)	— —
Salmo trutta	Brown trout	7	3·3	3·1	19·0	4·5	0·4	11·5 (2·6)	38·3 (3·9)	15·0 (7·8)	8·2 (10·1)	— —
Rhombus maximus	Turbot	4	2·1	3·4	15·1	2·1	0·3	8·9 (2·6)	21·7 (3·4)	26·6 (6·0)	21·9 (7·7)	— —

• Figures in parentheses represent molecular deficiency in hydrogen atoms.

Table 16. *Seasonal variations in fatty acid composition (% by wt.) of oil from herring.* (LOVERN, 1942)

Oil from herring caught in	*% oil*	*Saturated*			*Unsaturated**				
		C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
April	8·2	8·0	15·7	0·2	—	4·6 (2·6)	22·2 (2·9)	22·0 (3·9)	27·3 (4·2)
June	10·7	7·3	16·7	trace	0·6	7·5 (2·7)	21·1 (3·3)	27·3 (4·8)	19·5 (5·7)
June	15·7	7·5	12·8	0·1	0·3	7·0 (3·0)	21·1 (4·8)	30·0 (5·2)	21·2 (4·8)
July	20·7	8·3	12·1	0·3	0·5	6·4 (3·4)	21·0 (4·5)	28·3 (5·5)	23·1 (4·6)
October	18·8	7·3	13·0	trace	0·8	4·9 (2·7)	20·7 (4·2)	30·1 (4·6)	23·2 (4·3)
October	12·0	6·6	13·7	0·5	0·2	4·9 (2·8)	16·3 (3·6)	28·7 (4·4)	29·1 (4·1)
Calanus finmarchicus		8·3	10·6	1·3	1·6 (2·0)	11·8 (2·4)	16·8 (5·1)	23·5 (7·8)	25·1 (8·1)
'Average' marine fish					trace	10 (2·1)	25 (3·0)	25 (6·0)	15 (8·0)

* Figures in parentheses represent molecular deficiency in hydrogen atoms.

Table 17. *Component acids (% by wt.) of South African pilchard oils.* (BLACK and SCHWARTZ, 1950)

% oil content	*Iodine value*	*Saturated*						*Unsaturated**				
		C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
2·4	202·6	trace	5·6	13·1	1·4	0·6	0·3	2·3 (2·0)	17·6 (3·0)	16·2 (4·3)	26·8 (8·8)	16·2 (10·7)
15·7	196·5	—	6·7	17·4	2·1	0·4	0·3	1·9 (2·0)	15·0 (3·5)	19·8 (4·1)	25·8 (9·4)	10·6 (9·2)
10·5	187·3	—	6·9	17·3	2·1	0·5	0·1	1·9 (2·0)	14·6 (3·2)	19·3 (3·9)	26·3 (8·8)	11·0 (9·0)

* Figures in parentheses represent molecular deficiency in hydrogen atoms.

The fatty acid composition of oils from thin, fat and medium pilchards (*Sardina ocellata*), reported by BLACK and SCHWARTZ (1950), are given in Table 17. They suggest a preferential consumption of the short and medium-length fatty acids.

In general, one is not too greatly concerned commercially with the differences in fatty acid composition that may exist among the oils from different parts of a fish, for one either recovers *all* the oil from *all* the parts available of a given fish,

Table 18. *Comparison of fatty acid composition (% by wt.) of herring body oil and herring visceral oil (Clupea harengus).* (LOVERN, 1938; HILDITCH and PATHAK, 1948)

Source	*Yield* (%)	*Unsap.* (%)	*Saturated*			*Unsaturated**				
			C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Body oil	15·7	1·2	7·5	12·8	0·1	0·3	7·0 (3·0)	21·1 (4·8)	30·0 (5·2)	21·2 (4·8)
Visceral oil			5·8	15·7	2·8	1·4 (2·0)	10·5 (2·5)	31·7 (2·6)	22·4 (7·1)	9·3 (10·5)

* Figures in parentheses represent molecular deficiency in hydrogen atoms.

Table 19. *Fatty acid composition (% by wt.) of oil from different depots of tunny (Thynnus thynnus).* (LOVERN, 1936).

Depot	*Saturated*			*Unsaturated* *			
	C_{14}	C_{16}	C_{18}	C_{16}	C_{18}	C_{20}	C_{22}
Flesh	4·2	18·6	3·5	6·2(2·7)	26·0(3·2)	23·5(5·5)	18·0(6·8)
Liver	0	17·9	8·9	3·4(2·5)	23·5(2·8)	28·2(5·5)	18·1(7·4)
Pyloric caeca	3·4	18·4	2·7	6·3(2·7)	21·9(3·7)	25·5(5·5)	21·8(6·2)
Spleen	0	21	7	7 (>2)	27 (3·1)	22 (5·4)	16 (?)
Heart	0	25	3	4 (>2)	26 (3·4)	25 (5·4)	17 (7·5)

* Figures in parentheses represent molecular deficiency in hydrogen atoms.

or one recovers the oil from one particular part because of the presence of something special in that part. Thus a whole herring is reduced, or the parts of a salmon not canned go to the reduction plant, or a halibut liver is removed and the oil recovered because of the vitamins A and D found in the oil. As a result not very much is known of the variations in composition of oils removed from different parts of a fish.

Herring visceral fat, investigated by HILDITCH and PATHAK (1948) was materially different in composition from the depot fat, and was similar to typical marine fish liver fats (Table 18).

LOVERN (1936) published analyses of the oils extracted from various parts of the tunny (*Thynnus thynnus*), and the results are shown in Table 19. Lovern suggests that the oil from the caeca most nearly resembles the oil of the food of the fish in composition, and that the oil from the liver is the final composition of oil in this fish. He postulates that this shift in composition is the result of hydrogenation of some of the C_{18} and C_{16} unsaturated acids to stearic and palmitic acids; and that this is an adaption of the fish to the warm water in

Table 20. Effect of time and place of catch upon unsaturation of oil from Sardinops caerulea. (*From* BAILEY *et al.*, 1952)

Date (1937)	*Iodine value*	
	Northern California	*British Columbia*
Aug. 1–4		176·7
7–11		175·8
13–20		176·2
16–21	185·0	
22–28	186·8	
28–Sept. 2		176·3
28–Sept. 4	182·4	
Sept. 3–7		173·0
7–14		177·0
12–18	188·4	
14–19		175·5
Sept. 27–Oct. 2	189·5	
Oct. 3–9	188·4	
13		178·2

which it lives, and to its body temperature which is above that of the surrounding water.

On the other hand, analyses of oil reduced from *Sardinops caerulea* (known as sardine in California and pilchard in British Columbia, the extreme ends of its annual migration before this fish virtually disappeared) indicate an increased saturation during its northward migration (Table 20). This is the reverse of the change described above, and is the reverse of what might be expected on postulating adaptation to temperature. Possibly changes in diet of the fish during this northward migration may explain the observed change.

Recent work from the laboratory of SHORLAND (1953) has demonstrated the presence in various land animals of fatty acids with odd numbers of carbon atoms in the molecule, containing a methyl side chain. They have not reported on the presence of such fatty acids in fish oils. However, it has long been known that certain marine mammal oils contain *iso*valeric acid, unique in fats and oils both for the presence of a side chain and for its extreme brevity.

C. Glyceride composition

The pattern of distribution of the many fatty acids of a fish oil among the molecules of that oil is a problem which has not yet been solved. Various hypotheses have been advanced to account for experimental observations, of which only the first to be quoted is no longer credited. This first theory pictured simple glycerides each of which contained only the one kind of fatty acid until all that fatty acid was used. A second picture, that of 'even' distribution, gives a rational explanation to the arrangement in many vegetable fats. According to it, each fatty acid is distributed among as many glyceride molecules as possible. Thus,

Table 21. *Fatty acid composition of crystallization fractions of Icelandic herring oil.* (*After* BJARNASON and MEARA, 1944)

Fraction	*% by wt.*	*Saturated*					*Unsaturated**					
		C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
A	13·5	—	12·0	22·0	2·6	0·6	0·7 (2·0)	4·4 (2·0)	12·3 (2·3)	16·9 (2·6)	28·5 (2·5)	—
B	19·5	—	9·7	15·5	1·5	0·1	1·2 (2·0)	9·2 (2·0)	15·9 (2·7)	23·1 (3·1)	23·8 (2·9)	—
C	17·3	—	6·5	13·1	1·0	—	1·0 (2·0)	11·5 (2·4)	20·1 (3·1)	27·3 (5·1)	19·5 (3·5)	—
D	19·0	0·2	7·4	10·9	—	—	1·3 (2·0)	13·8 (2·3)	21·0 (4·0)	27·9 (5·9)	20·1 (5·0)	—
E	30·7	0·1	4·2	5·0	—	—	1·4 (2·0)	15·8 (2·6)	24·1 (4·3)	29·7 (7·2)	19·3 (6·6)	0·4 (3·8)

* Figures in parentheses represent molecular deficiency in hydrogen atoms.

Table 22. *Glyceride composition of Icelandic herring oil.* (*After* BJARNASON and MEARA, 1944)

Glyceride	*Mol. %*
Disaturated, mono-unsaturated (mono-ethenoid)	3·7
Mono-saturated, di-unsaturated (mono-ethenoid)	28·3
Mono-saturated, di-unsaturated (mono- and poly-ethenoid)	32·7
Tri-unsaturated (mono-ethenoid)	1·4
Tri-unsaturated (mono- and poly-ethenoid)	33·9

until a given fatty acid exceeds 33 mol. per cent two molecules of it will not be found in any one glyceride molecule. The work of Hilditch and his school has offered much data to substantiate this hypothesis. It is particularly applicable to seed fats. BJARNASON and MEARA (1944) separated a sample of Icelandic herring oil into five fractions by crystallization from acetone at different temperatures (fraction A being the least soluble), and then performed a fatty acid analysis on each fraction. Table 21 shows that all fatty acids were found in most of the glyceride fractions. Palmitic and stearic acids were found even in the most soluble glycerides, and unsaturated fatty acids occurred in the most insoluble glycerides. From these data the composition of the glycerides was calculated to be probably as shown in Table 22. The authors conclude that their results exemplify the principle of general even distribution of fatty acids among the glycerides of a marine animal oil.

A third concept is that of 'random' distribution in which the fatty acids arrive in any given glyceride molecule by chance. Thus a simple glyceride, in which three molecules of one fatty acid are present, is theoretically possible on a statistical basis.

Each of these theories explains rationally the composition of a fair number of

oils, and fails to fit the experimental determination of others. A more recent theory, that of 'partial random' distribution, has been advanced to explain the fatty acid arrangement in corn oil, a simple oil containing only four fatty acids, which does not fit either of the preceding theories. The experimental observations fit this theory better than they fit the others. These theories have been discussed in detail recently by VAN DER WAL (1955).

It follows that the 'cold-clearing' of a fish oil, i.e. removal of the portion of an oil which solidifies at a given temperature (stearine), cannot produce a saturated stearine since the chances of a molecule in a fish oil being saturated are remote. The molecules containing the greatest proportion of longest chain, least unsaturated fatty acids will be the first to crystallize out. Many saturated fatty acids will be left in the oil because of their association in glyceride molecules with unsaturated fatty acids. This is made evident in an experiment in which was measured the saturated fatty acid content of the stearine and of the cleared oil obtained from samples of pilchard oil (*Sardinops caerulea*, BAILEY *et al.*, 1952). Complete separation of saturated and unsaturated fatty acids by cold-clearing of an oil is clearly not possible, and this is demonstrated in Table 23. When even a third of the oil was removed as stearine, over half the saturated fatty acids were left in the cold-cleared oil.

Even this apparently minor effect of cold-clearing on removal of the more saturated fatty acids has an important effect on properties of the oil. Removal of stearine greatly increases the rate of drying (hardening) of pilchard oil as shown in Table 24. The hardness of films of oil on metal plates was measured in an apparatus developed by BROCKLESBY and DENSTEDT (1931). The figures given are each an average of 60 measurements. Removal of stearine also increases

Table 23. *Saturated fatty acid content of stearine and of cold-cleared pilchard oil obtained at several temperatures.* (*Calculated for* 100 *g samples from data in Table* 35*A*, Fish. Res. Bd. Can. Bull. 89, 1952).

Temp. of crystallization (°C)	−2	−5	−10	−15	−20
Stearine removed (%)	10·2	14·9	16·0	21·7	34·3
Iodine value of cleared oil	190·6	190·8	195·4	197·5	205·6
Satd. fatty acids—in stearine (g)	4·0	5·4	5·6	7·5	8·7
—in cleared oil (g)	15·4	13·9	12·8	11·2	10·4
—total (g per 100 g oil)	19·4	19·3	18·4	18·7	19·1

Table 24. *Effect of stearine removal on degree of drying of pilchard oil* (BROCKLESBY and DENSTEDT, 1931).

Stearine removed (%)	0	1·0	7·1	10·0	21·4
Hardness (g)	28·5	36·3	42·3	51·6	72·0

the degree of polymerization that is possible. This was shown by BEHR (1936) who demonstrated increased viscosities of polymerized sardine oils first subjected to increased degrees of cold-clearing. Brocklesby arrived at the same conclusion by measuring the increases in molecular weight resulting from polymerization of samples of pilchard oil first subjected to increasing degrees of cold clearing (BAILEY *et al.*, 1952).

Removal of stearine prevents the development of a cloudiness in polymerized pilchard oil. This cloud may result from deposition of stearine (BAILEY *et al.*, 1952), from the decreased solubility of the more saturated glycerides in polymerized oil (MATTIL, 1944), or to some interesterification during polymerization resulting in the formation of more saturated glycerides.

D. Properties

Fish oils are liquid or semi-liquid at room temperature. The temperature at which solid (stearine) formation commences is a variable character, even among oils from one species. The temperature of complete solidification is very much lower. At intermediate temperatures the oil is a 'slush' of crystals of stearine suspended in oil. The viscosity of a fish oil is very dependent upon temperature, decreasing as the temperature rises. It varies between about 25 and 50 centipoises at 25°C. Fish oils are lighter than water, with specific gravities a little greater than 0·9 at room temperature. Since they all expand on warming, they become lighter with rising temperature. The coefficient of cubic expansion is about 0·0007 to 0·0008 per °C. Stearine possesses a similar coefficient but the change from solid stearine to liquid oil at the same temperature is accompanied by an increase in volume, which increases markedly the coefficient over that range of temperature.

Fish oils are mixtures of esters, formed by the combination of glycerol with fatty acids (three per molecule). They therefore exhibit the reactions of esters, of which possibly the most important is hydrolysis. This may be accomplished in various ways—deliberate or accidental.

Most of the fatty acids in most fish oils are unsaturated. This property may be put to deliberate or accidental use—deliberate in the processes of hydrogenation, oxidation, polymerization, condensation, sulphation, sulphonation, sulphurization, hydroxylation, halogenation, and elaidinization; accidental in the process of oxidation when it produces a rancid oil.

Details of the properties of fish oils are discussed in various places, e.g., *Fisheries Research Board of Canada Bulletin* 89. New oils are reported frequently in the *Journal of the American Oil Chemists' Society*.

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6

THE PRODUCTION OF MARINE OILS

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6

THE PRODUCTION OF MARINE OILS

H. N. Brocklesby and J. R. Patrick

I. Introduction

It is not the purpose of this section to go into details of the many processes that have been used or devised for the production of fish oils. Rather the aim is to outline the general trend of development and to point out the factors that influence these trends.

In general, the development of processes for the production of fish oils has been slow and sporadic. Because of their peculiar make-up, fish oils, except in a few specialized instances, usually occupy a low rung on the ladder of utilization and are among the first to be affected by market fluctuations. With the present abundance of fats and oils on the world markets, fish oils (at least in the United States) are in limited demand and the incentives to work out more efficient and better methods of production are conspicuous by their absence.

Changing areas of production is another reason for sporadic attempts at improvement. A few years ago the United States Pacific Coast was a large producer of fish oils and at the same time much of the process development centred in that area. With the lack of fish, the plants are now practically idle, and interest in production methods is no longer found. The rising importance of other areas of fish meal and oil production have also transferred the areas of activity with regard to the development of better production methods. The change in areas also brings about different approaches to the problem. One of the greatest drawbacks to capital investment in a fish meal and oil plant is the short season of use. In the United States the tendency has been to build plants that would have sufficient capacity to take care of the glut of fish during the height of the production season without undue delay. While tending towards the production of first-quality merchandise insofar as such quality is influenced by freshness of raw material, this tendency certainly emphasized the high overhead cost of such plants and acted against any frequent change in plant design.

In Europe, and particularly in Norway, on the other hand, the tendency has been to store the raw fish during period of glut and to run them through much smaller plants operating over a longer period of time. This approach would indeed be ideal if a cheap and effective preservative could be found that would inhibit depreciating quality of the raw material (with consequent decreasing plant efficiencies and decreasing quality of the finished product). Such a preservative has yet to be devised.

With such limiting factors in operation, what progress has been made in meal and oil production processes has had, as a main theme, not the more efficient production of a better oil but the more efficient production of a better

quality fish meal. As an example of changing conditions, consider for a moment the situation of fish liver oil producers. Fish liver oils were produced solely for their vitamin A and D content. First the vitamin-D-containing livers (percomorphs) rapidly faded out of the economic picture with the commercial introduction of synthetic vitamins D_2 and D_3. The successful introduction of synthetic vitamin A has now all but written 'finis' to the halibut, cod, dogfish and other fish liver industries whose main product was vitamin A. As a consequence, any new methods applied to these industries must by sheer necessity, produce some other marketable item from the raw material and supply the vitamin A oil solely as a cheap by-product, or the livers must be available as a by-product of another activity. Our review of liver oil processes will therefore be very brief and somewhat academic. Although not quite so marked as in liver oil processing, the switch in interests in fish meal and oil plants from oil production to fish meal and growth factor production is readily discernible.

II. Production of Fish Liver Oils (Vitamins A and D)

Most liver oil processes have been designed to give high yields of oil even though high oil yields do not necessarily mean high yields of either vitamin A or D. The processes are conveniently divided into those for livers of high oil content and those for livers of low oil content.

Livers of high oil content were originally processed simply by allowing the livers to rot in wooden barrels, a process that was superseded by simple steaming and skimming. The steam process was in vogue for cod liver oil production up to the time when synthetic vitamin A practically stopped the industry. A modification of the steaming process much used by dogfish oil producers of the Pacific coast was to macerate the livers to a fine brei and then to treat them with live steam until liquefied. The mixture was then put through two-phase or three-phase centrifuges to separate the oil. In a modified method the oil was allowed to separate by gravity after steaming and the residual aqueous liver material then treated with 2 per cent sodium carbonate or 1 per cent sodium hydroxide and again heated until the liver material liquefied. It was then separated in a suitable centrifuge. In all cases the attempt was made to liquefy completely the liver protein and thus release all the oil and associated vitamins.

That vitamins A and D are not entirely associated with the oil *in situ* in the liver has been shown by many investigators. Thus, in the above process, the alkali-treated liver material usually yields an oil higher in vitamin A potency than that obtained by simple steaming. Treatment of livers with common salt or with calcium chloride will release an oil low in vitamin A. Subsequent treatment of the residual liver material with alkali will give an oil high in vitamin A. Such experiences have demonstrated that a part at least of the vitamin A is associated with the cell tissues.

Other lesser known methods for extraction of oil from livers of high oil content include freezing and pressing of the frozen livers, treatment of the livers with dry materials with high moisture absorbing properties (such as dry beet pulp), freezing of the livers before steaming, acid treatment of the livers before

steaming, enzyme digestion of the liver protein and finally, vacuum cooking of the livers. All of these have been used commercially in the last two decades. Steaming of the livers, with or without alkali treatment, followed by centrifugal separation of the oil is the common method now being used in places where vitamin oils are still being produced.

Processing of fish livers of low oil content such as halibut, ling and black cod, the percomorphs, etc., calls for modified techniques. When the high vitamin potency of these oils was first recognized, pharmaceutical companies used elaborate techniques for the removal of such vitamins. Included in these processes were a variety of solvent extraction methods, usually involving the heat-coagulation of the liver protein and removal of a part of the aqueous liquor. A variety of solvents were used but the products had a common fault, they were highly coloured and had disagreeable odours and after-tastes. Enzyme digestion of the liver proteins gave an improved yield of vitamins and a bland oil, but the process proved to be rather costly and difficult to control. Alkali digestion of the liver proteins under carefully controlled conditions proved to be the most satisfactory method, and ultimately practically all the high potency liver oils were recovered in that manner. Elaborate and closely guarded techniques were used to control the protein digestion, in order to avoid saponification of the oil and the formation of troublesome emulsions. In addition, several ingenious methods for working in oxygen-free media were devised, with the object of producing high vitamin yields, and oils with a low peroxide number. In those areas where the processing of low oil content livers is still economical, modifications of the alkali digestion process are still being used. Due to the fact that a clear non-colloidal solution of proteins is seldom achieved, it is practically impossible to recover all the vitamin oil in such a mixture, even with the most efficient of centrifuges. This has led to the use of the so-called pick-up oils. After the original liver oil has been recovered, an oil of low potency is added and thoroughly mixed with the aqueous phase. This is then separated off and the process repeated until practically the theoretical amount of the vitamins in the original livers has been recovered. By using oils of decreasing potency in each subsequent step, and advancing these oils one step in the next batch, a process similar to a counter-current extraction process is achieved and a high vitamin recovery thus realized. Centrifuges play a very important part in these processes. For a description of the types in common use the reader is referred to *Bulletin* 89 of the Fisheries Research Board of Canada or to *Fishery Leaflet* 233, Fish and Wildlife Service, United States Department of the Interior.

A brief mention may be made of two novel processes devised chiefly for the recovery of high-grade cod liver oil. In the first a particular type of preservative containing ethyl or *iso*propyl alcohol, with or without the addition of a small amount of acetic acid was found to be particularly effective. Three solutions were investigated in some detail (Kaufman, 1945). These were (a) 10 per cent alcohol containing 1 per cent acetic acid, (b) 20–25 per cent alcohol solution and (c) a 35–50 per cent alcohol solution. Either ethyl or *iso*propyl alcohol was found to be effective. The preservatives were mixed with livers in a proportion

of 2 parts of livers to 1 of preservative. When preservative (a) was used in a 40 day test at room temperature no odours developed with either ethyl or *iso*propyl alcohol, very little volatile nitrogen was produced, free fatty acids in the oil increased to about 9 per cent, the proteins of the liver were completely digested and a good yield of oil was obtained with the same vitamin potency as the original oil. From a preserving standpoint this mixture was very good, allowing proteolysis to take place and considerably reducing the activity of the lipases. However, the oil recovered was very dark and required alkali-refining. With an increase in alcohol, as in mixtures (b) and (c), the lipolysis of the oil was greatly reduced, with up to 20 per cent alcohol in the preservative solution, proteolysis progressed satisfactorily. The colour of the oil with these concentrations of alcohol was considerably improved and vitamin yields were excellent. Higher amounts of alcohol inhibit proteolysis and make the subsequent treatment of the livers rather troublesome. It is claimed that alcohol concentration in the range of 30–35 per cent of the preservative is critical for proteolytic enzyme action. This type of approach to preservation and processing may hold some possibilities for development with fisheries raw material other than fish livers.

Another novel method that may have more general application is that of Van den Heuvel (1952) who minces fish livers and adjusts the pH to about 8. On heating to 55–60°C. the mixture suddenly changes from a semi-solid to a liquid. Hydration of the protein takes place, setting the oil free so that the material is now a suspension of hydrated protein floating in the liver oil. Application of this method is apparently restricted to fresh livers, as trials on frozen and preserved livers were not very successful.

III. Production of Fish Body Oils

A. Older processes

By fish body oils we include sardine, menhaden, herring, salmon, anchovy, mackerel and other species which are commonly processed for the manufacture of fish meal and fish oil. The oil recovery from these species may vary from 8 to 45 gal/ton depending on the sexual or feeding cycle of the fish.

Early methods of handling fish waste consisted chiefly in batch cooking and pressing in hydraulic presses fitted with canvas cloths. Poor oil yields and a high oil content meal were obtained. With the growing demand for a high quality fish meal in the animal feeding industry, these batch processes proved to be uneconomical for handling large tonnages quickly, and the present-day modern continuous plant gradually evolved. Although still far from perfect with respect to quality of protein feedstuffs they produce, these plants are capable of handling huge volumes of fish, capacities of up to 20 tons/h being quite common.

Essentially, the continuous plants consist of a continuous cooker which may be either a steam jacketed or plain tube through which runs a spiral conveyor. Steam is injected at regular intervals along the lower side of the tube and the

flow of fish into the front end of the cooker forms its own seal. Pressures in the cooker are kept low, from 3 to 5 p.s.i. being common. The object is not to overcook the fish or scrap but simply to coagulate the protein and cause release of the oil. From the cooker the material passes into a continuous screw press where it is subjected to high pressures by a series of screws, the oil and water being forced through the curbs. These curbs are usually perforated metal screens backed by heavy metal straps, the perforations being tapered with the small openings on the inside to prevent clogging. The oil and water mixture coming from the presses contains suspended solids. These solids are removed by passing through a cylindrical rotating screen, the accumulated solids working their way out of the end of the screen. They are further pressed in a small continuous 'foots' press after which they are admixed with the bulk of the press cake and fed to the continuous drier. A great deal of attention has been given fish meal driers within the last few years with particular respect to lower drying temperatures, more efficient heat exchange and better dust recovery.

The oil and aqueous phase coming from the rotary screen may now be separated in a variety of ways. In older plants series of settling tanks are still in use. These tanks are arranged in cascades, the first one being provided with steam coils where the emulsion of oil and aqueous phase is broken. The oil-rich upper layer in the first tank flows into the second tank where the upper layer becomes still richer in oil and so on down the entire cascade. Each tank is of course provided with outlet valves. Modern plants have replaced settling tanks with an array of centrifuges. Usually the oil mixture coming from the rotating screen goes first to a surge tank where it is reheated to 190–200°F. It is then fed into a continuously desludging centrifuge that separates the mixture into an oil still containing a small amount of water. The aqueous phase from the centrifuge contains about 1 per cent oil.

The wet oil is then passed through a clarifier centrifuge, where the moisture content is reduced to 0·5 per cent or less, and is then stored. The aqueous phase coming from the desludging centrifuge contains from 6 to 8 per cent dissolved solids, largely gelatin proteins and protein breakdown products. This liquid is condensed in double- or triple-effect evaporators to 50 per cent solids to form the commodity 'condensed fish solubles'. The hot condensed material is sometimes run through centrifuges where a portion of the residual oil is recovered as a black and somewhat thick product.

The major variables in fish oil quality are free fatty acids, colour and insoluble impurities. These are largely a function of the quality of the fish being processed. Fresh fish will yield a press water that is easy to 'break' and the resulting oil will usually run less than 2 per cent free fatty acids and will be from light amber to light yellow in colour. Lipolytic enzymes are very active in fish, especially at room temperature, with the result that high free fatty acids are produced which tend to promote stubborn emulsions. This prolongs processing times with the result that dark oils high in free fatty acids, moisture and impurities are produced.

Usually fish oils as produced from fresh materials are quite free of peroxides,

although it is quite likely that incipient oxidation has already taken place. It is in storage, however, that most fish oils progress to the more or less rancid state. Fish oil storage tanks quickly become coated with an oxidized layer (linoxyn) that is a very efficient catalyst for further oxidation. If the oil going into the storage tank is quite dry (less than 0·5 per cent moisture) then little change in free fatty acids will be found. In actual practice, however, and particularly with large storage tanks, it is almost inevitable that sooner or later a wet oil or one highly contaminated with wet dispersions of proteinaceous material will be pumped into dry oil. Free fatty acids will then increase rapidly.

B. New processes

In an effort to improve the nutritional value of the fish meals, some new processes have recently been developed. Some of these are still in the development stage but some are in actual production. With the rapid adoption of solvent extraction by the soybean and cottonseed industries and the technical developments that have been made in such plants during the past few years it is obvious that such methods should be tried out on fish meal and oil production. In the past there have been many attempts to develop a continuous solvent extraction process for fish reduction. Nearly all of these have failed, due chiefly to (1) high initial costs (2) inadequate engineering (3) high operating costs and (4) low capacity. One drawback to solvent extraction of fish material is the high water content. For efficient extraction with most solvents, this must be reduced to a point where the protein mass is more or less cohesive but at the same time must be permeable to the solvent. In most of the attempts that have been made to design small self-contained units, the designers have purposely avoided inflammable solvents such as hexane. Chlorinated solvents have been tried, and in at least one case with which the writers have had experience, a 2 ton per hour plant operated fairly satisfactorily, but the problems that would have to be solved in order to expand the unit to handle large amounts of raw material made the project uneconomical.

An interesting plant for solvent extraction of fish material has recently been constructed in Iceland. The raw material is charged into vacuum cookers together with additional herring oil. It is claimed the herring oil assists in heat transfer. The cooking and drying continues until the protein matter coagulates and is dispersed in a continuum of oil. In this condition it is easily pumped. The bulk of the oil is then removed in sludging centrifuges or alternately, in vacuum filters. The 'dry' cake or sludge, containing about 45 per cent oil is then transferred to a continuous solvent extractor in conventional soybean extraction equipment and is stripped of oil with hexane. Solvent removal from the meal and from the oil follows the conventional pattern of seed cake solvent plants. Unfortunately, no operating information is yet available for this installation. For economical operation, this plant requires from 600 to 700 metric tons (660–770 U.S. tons) per day of herring or 400 tons of rosefish. Since its completion there has not been a sufficient quantity of either type of fish to warrant operation.

A method for oil and fat recovery involving azeotropic distillation has recently been patented by LEVIN (1950). This process uses either heptane or trichlorethylene. The application of the process to fish is described as follows: The raw fish is first put through a disintegrator and then into a 'continuous agitator' where the material is heated with agitation in the presence of the solvent. This is stated to be an essential part of the process because the fish material forms small discrete particles that will not stick together during later processing. The slurry then moves into a continuous solvent cooker which consists of a long horizontal jacketed trough with a vapour collecting space above leading to condensers. Heat is applied and solvent and water distilled off, the solvent always being maintained in excess. The miscella is drawn off from this cooker, and after passing through a filter, is steam stripped in a conventional solvent recovery still. The solids discharged from the cooker are then passed into a continuous drier where the remaining solvent is removed and the meal sacked. The inventors of this process emphasize the granular form of the protein solids (which they claim reduces dust hazards) and the clear miscella that is obtained which allows of conventional equipment for steam stripping the solvent. Sufficient data are not available to assess this method from a practical standpoint.

A mechanical rendering process (I. H. CHAYEN, 1953) which involves the use of mechanical shock waves to break up the oil cells has been proven practical in rendering fats from bone. The inventors are now attemping to adapt the process to fish livers and to oily fish. While the application of shock waves undoubtedly will break up the oil cells in fish tissues the subsequent recovery of such oil from the tissues will still present quite a problem. If the separation can be accomplished without further dilution of the treated fish with water (in the application to fat recovery from bone 7 parts of water are added to 1 of bone) then the process may have some definite interest to fish meal producers. The outstanding feature of the process is the very short processing time (about 5 min) and the fact that since no heat is used in the process, fats and oils produced are of very high quality. The method is particularly useful for removing oil from cellular material and should therefore find use in the rendering of whale oil from blubber, the latter being far more tough and fibrous than tissues of fish.

In those countries where the production of fish oils is important to the national economy a very different approach is being made to methods of production. In Norway for instance, where production of herring meal and oil is an important industry, the raw material is stored in large bins or pits for perhaps as long as several weeks, with no preservative other than a little salt. In this case the glut occurs during the winter time, so the low temperature tends to retard spoilage. By such storage, it is possible to use plants of small capacity and to use them over a longer operating period. In other localities, however, this method is not applicable as putrefaction proceeds so rapidly that poor products are obtained and the operating plants constitute a public nuisance because of the odour. In Great Britain, where attempts are being made to

build up the herring meal and oil industry, considerable effort is being given to the possibility of adapting the alkali digestion process, so widely used in the liver oil industry, to the preservation and processing of herring. From an oil production standpoint, the process leaves little to be desired. Briefly, the fresh fish are run through a hasher and mixed with an equal part of water and 3 per cent sodium hydroxide (based on the weight of the fish). If this mixture is stored in closed tanks it will keep free of bacterial action for very long periods. If exposed to the air it will slowly release ammonia. The alkali seems therefore to provide a means of storage during a glut period and allow the material to be processed in smaller plants on a more stable schedule.

The alkaline mixture is heated to 90°C and then transferred either to settling tanks or run through centrifuges. In full-scale equipment, the digestion tank is used on a continuous basis, the raw alkaline fish moving in at the bottom, heated by direct steam and overflowing from the top to settling tanks or centrifuges. In treating fresh fish for immediate processing, it has been found advantageous to allow the cold alkali-treated fish to stand in the cold for about 12 h before running through the digestor. By the use of this alkali process excellent yields of oil have been obtained (Lovern, 1951, 1952) and since the oil is recovered from an alkaline medium, the oil is really an alkali-refined product.

Whether or not this method will finally be adopted for large-scale use depends entirely on the recovery and value of the alkali-treated protein fraction. If loss of nutritive value brought about by racemization of the amino acids and actual loss of cystine and methionine can be reduced or controlled so that economic yield of high-quality fish meal can be produced then this process may solve many problems of fish meal and oil production in many parts of the world. It might be added, that the alkali digestion process has already been used on a limited scale for the production of salmon oil from salmon canneries in Alaska. In this case the aqueous alkali phase is discarded.

A process of treating raw fish and fish waste that is meeting with some success in California involves a multi-stage enzyme process that quickly converts the raw material into a fluid product that readily releases oil when centrifuged. Oils obtained by this process are light coloured and very low in free fatty acids, usually less than 0·5 per cent when fresh material is processed. The important feature of the process is that the nutritive value of the protein phase is maintained equal to that of the raw material.

IV. Production of Whale Oil.

The blubber of whales differs greatly from the tissues of fish and the processes required to free the oil from such blubber are much more drastic than those required for fish. Pressure cooking with live steam is the essential feature of whale oil rendering.

Horizontal rotary pressure cookers are gradually replacing all other types of cookers in the whaling industry. They are built to stand pressures up to 100 p.s.i. They consist of a heavy iron tank inside which there is a perforated iron cylinder

attached to a heavy shaft that protrudes from the cooker through stuffing glands. The perforated cylinder within the extractor has open ends and is slowly rotated during operation. The blubber, previously converted into a brei by passing through heavy metal corrugated rolls, is fed into the extractor by means of two pre-heaters, one at each end of the extractor. The tops of these pre-heaters are usually flush with the deck of the processing ship and the blubber brei is fed into the pre-heaters until they are full. A quick-closing pressure cap is then closed and steam turned into the pre-heater. The pre-heater is isolated from the main extractor by means of a pressure valve that opens when the pressure in the pre-heater rises above that in the main extractor. When the brei has been forced into the extractor entering at both ends directly into the center of the rotating cylinder, the pre-cookers are again isolated, opened and refilled with another charge of brei. The combined action of the high temperature and the rotary motion in the perforated cylinder gradually releases the oil and a fine slurry of connective tissue in water, and this is periodically bled from the bottom of the extractor through a pressure valve. The oil is separated from the aqueous gurry by means of sludging separators, finally passing through polishing centrifuges and thence to storage.

Whale bones are de-oiled in much the same manner with the exception that they are first broken into small chunks before entering the extractor. Whale meat is processed for whale meal and meat oil by equipment identical with that used for the wet rendering of fish. Whale livers are now being extracted for their vitamin content. Alkali digestion and solvent extraction are the two methods most frequently used.

Whale oil production is largely carried out on board large mother ships that are isolated from sources of supply for six months or more. Equipment to handle whale products must therefore be ruggedly built to stand full-time operations for months at a time. With these limitations in mind, together with the necessity for huge throughput capacities, it is readily seen that new processes will be adapted only slowly. If however, any new process can be shown to save on the tremendous steam requirements of the present methods, such a method is bound to create some interest.

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THE UTILIZATION OF FISH OILS

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THE UTILIZATION OF FISH OILS

H. N. Brocklesby and J. R. Patrick

I. Introduction

Fish oils do not enjoy complete interchangeability with all other fats and a quick glance at the composition data given in Chapter 5 will explain the reason for this. Fish oils of commerce are chiefly body oils, such as herring, pilchard (sardine) and the like. They contain considerable saturated and partially saturated fatty acids distributed in the glycerides in a manner that does not allow of a very precise separation of the saturated from the unsaturated by physical means. Thus, while refrigeration of raw fish oils into 'stearine' and 'cold-cleared oil' gives a product that will not deposit further stearine on standing, such a cold-cleared oil still contains considerable saturated fatty acids. Peculiar differences between the unsaturated fatty acids of fish oils and those of vegetable oils also contribute to differences in behaviour. The polyethylenic acids in vegetable oils are largely restricted to the C_{18} series but those in fish oils range from C_{16} to C_{26} with the C_{20} and C_{22} series predominating. Again we find a difference in the actual structure of the unsaturated acids. Polyethylenic acids of vegetable oils have the first double bond in the 9–10 position and the double bonds are usually separated by one methylene group, or, as in elaeostearic acid, are conjugated. In fish oils, although some unsaturated acids are similar in structure to those in vegetable oils, there are also unsaturated acids with the double bonds separated by two methylene groups. This difference in structure is most likely the reason for dissimilar chemical properties.

II. Dietary Use of Fish Oils

Raw and processed fish oils have been and are being used in certain food applications. In the past, considerable amounts of cold-cleared fish oils have been used in animal feeds as carriers of oil-soluble vitamins. With the advent of synthetic vitamins A and D the use of vitamin oils has dropped off considerably. However, there is evidence that under certain conditions fish oils again may be utilized in animal feeds.

A. Use in human foods

It has been the practice in some quarters to add salmon oil to canned salmon for markets demanding an oil-rich product. The salmon oil so used is very carefully processed from fresh salmon cuttings and does not include any visceral material. Immediately after production, the canning oil is placed in airtight containers and, in some cases, is immediately refrigerated. The use of such a canning oil enables the canner to maintain a uniform product irrespective of

the variation in oil content of the raw material. Salmon-roe oil is sometimes added to intensify the red colour.

In Norway, herring or cod liver oil is now specifically processed for use in the canning of sardines, anchovies, etc. The process is one of polymerization followed by steam deodorization. From the specifications given for this oil in an article by HAMM (1947) it can be deduced that polymerization is carried to the point where most of the polyunsaturated fatty acids have at least been dimerized. This would confer a certain amount of stability against oxidation and rancidity and, of course, would considerably increase the viscosity. While under specific situations the use of such a polymerized fish oil might be advantageous, it is doubtful if it would ever become generally attractive from an economic or nutritional standpoint.

It must be pointed out that we do not have sufficient evidence with regard to the metabolism of polymerized oils as yet to consider the wholesale use of such materials in foods. Inasmuch as emulsification is a necessary preliminary step to absorption it can be postulated that polymerized oils would not be so readily absorbed as the non-polymerized. LASSEN, BACON and DUNN (1949) found that with rats on a diet containing 5 per cent of the oil, increasing the amount of polymerization decreased the coefficient of digestibility. Molecular weight determinations of the fatty acids of the fæces showed that little if any of the polymerized acids was absorbed. Where the amount of such polymerized oils ingested is low, there would probably be no harm in their use. If the amount consumed is large, however, the effect would be similar to that obtaining when large amounts of mineral oils are ingested and would result in secondary effects such as interference with the absorption of fat-soluble vitamins. Although some recent work on humans (MATSUMURA, 1951) has indicated no decrease in absorption coefficients of fish oils following polymerization, CRAMPTON *et al.* (1951a) reported a decrease in weight gains in rats fed with oils that had been heated to 275°C. These effects were noted for vegetable oils as well as fish oils. In later papers, CRAMPTON *et al.* (1951b, 1953), these groups concluded that the reduction in nutritive value of heated oils was due to the presence of dimerized fatty acids and also to the destruction of essential fatty acids. ROY (1944) has also shown that with both animal and vegetable oils the coefficient of digestibility begins to decrease when the temperature of treatment is raised to 275°C. Below that temperature no measurable effect was detected. It is perhaps significant that 275°C is the temperature at which most oils begin to undergo definite polymerization.

B. Margarines, cooking fats and shortenings

In the United States fish oils in these food commodities have been utilized in very small amounts. For such use, the fish oils are hydrogenated to an iodine value that ensures stability against rancidity. This is not easy to accomplish. Even when oils such as herring or sardine are carefully hydrogenated with due regard to type and amount of catalysts and to temperature and pressure, *iso*-acid formation always occurs. If these oils are hydrogenated under

conditions usually found satisfactory for vegetable oils, i.e. to obtain a desirable melting point, *iso*-acids contents are too high, usually resulting in fats that will go rancid rather quickly.

Fish oils are therefore used for such purposes only under exceptional circumstances, i.e. when there is a scarcity of vegetable oils, and even then, are only used with great caution. A few exceptions have been noted from time to time. Such an exception is the use of a highly hydrogenated fish oil for shortenings intended for use by bread manufacturers. It has been claimed that such a shortening, by reason of its content of C_{20}, C_{22} and C_{24} fatty acids, confers a better crust on the loaves. Similarly, a cooking fat with a high proportion of hardened fish oil has been made in an attempt to reduce the smoke point of the heated fat when used in commercial deep frying processes.

In Europe considerable quantities of fish oils and whale oils have been used in the manufacture of margarine (see Chapter 10). This again was largely a matter of expediency brought on by war conditions. However, whale oil is still used for this purpose as it does not present the problems in hydrogenation to the same degree as do fish oils.

C. Use in animal feeds

Considerable amounts of fish oils have in the past been consumed by farm animals. These oils have not been consumed by deliberate addition as such but mainly as carriers of vitamins A and D and as residual oil in fish meals. With the growing conviction in the feed industry that in many instances the fat content of animal rations is too low, and the growing use of low-grade tallows and greases in such rations, suggestions have from time to time been made that fish oils should be of value in this respect. Great caution should be exercised in the use of fish oils in animal feeds. A brief look at the true picture would be salutary at this time.

It has been known for some time that the addition of vitamins A and D in a fish oil carrier to poultry rations involves major problems of stability, particularly the stability of vitamin A. The oil carrier is usually well dispersed over the feed and thus presents a very great surface to the oxygen of the air and contact with pro-oxidant materials in the ration The use of antioxidants to a certain extent gives greater stability, but in order to attain the desired stability the amount of antioxidants necessary is excessive.

The exact role that the fish oil carrier performs in the stability or non-stability of vitamin oils has never been completely determined. It has been recognized for some time that vitamin A stability varies with the nature of the oil or fat in which it is dissolved. The picture has been and still is complicated by the fact that the different kinds of oils and fats investigated have in themselves varying contents of natural antioxidants and it is quite possible that the variation in such antioxidants may be of more importance than the exact composition of the oil itself. Be that as it may, fish oils in general are not to be regarded as the ideal carrier media for vitamin A.

Attention has been focused on fish oils as a feedstuff constituent quite

recently by work in Connecticut on encephalomalacia in chicks (Singsen *et al.*, 1954). Working with a purified low-fat diet with chicks low in vitamin E it was found that fish oils introduced as a stress factor would invariably produce encephalomalacia. This excellent piece of work can possibly be grossly misinterpreted. While fish oils were indeed used in the experiment it is quite conceivable that other unsaturated oils could have produced the same effects. The encephalomalacia is not produced by the oils *per se* but by the destruction of vitamin E. It was demonstrated that a ration containing 2 per cent of fish oil and less than 3 I.U. of vitamin E per pound, would not produce encephalomalacia if 0·0125 per cent of an antioxidant, diphenylenediamine (DPPD) was used. It is thus possible to protect fish oils with antioxidants so that destruction of vitamin E does not occur. However, this may not be easy to accomplish in a practical manner. To be efficient, the antioxidant must be added to the fresh oil and not to one that has started to go rancid. Furthermore, much work still remains to be done to ascertain how long fish oils protected with various amounts of antioxidants will remain free of oxidation when added to the mixed dry feeds. Much work can be cited to show that freshly prepared fish oil added to poultry rations that were consumed within a few days of mixing did not exhibit any detrimental effects attributable to the oil. What would happen on storage of the feed for several months is still a moot point.

Some indication of the degree of loss of nutritive value when fish oils become oxidized in a ration may be gathered from the work on herring meal by Biely *et al.* (1951). These workers studied the effect of heating fat-containing and hexane-extracted herring meal on the growth of chicks. The results indicated that heating a non-extracted herring meal (oil content 7·5 per cent) for 120 min at 300°F definitely reduced the nutritive value while the similar treatment applied to the extracted meal (oil content approximately 0·3 per cent) had no effect. Extraction of the heated oily meal did not improve its nutritive value, but the addition of the extracted oil to a non-heated extracted meal again reduced the nutritive value of the latter to a degree equal to that obtained when an oily meal is heated. The data indicate that the changes in the oil during heating impair the non-oily portion of the meal in addition to producing some apparently toxic products in the oil itself. While it is realized that such heat-induced changes in herring oil may not be exactly parallel with the type of changes that take place in unheated oily herring meal or in rations containing unheated fish oils, nevertheless it is known that to a certain extent the sequence of events is similar.

Although the experimental difficulties are great, the above workers have shown that, under certain conditions, a definite decrease in nutritive value of an oily fish meal will take place on storage. An oily meal produced in a regular commercial plant will deteriorate on storage, but a meal dried by low-temperature drying will apparently not deteriorate. So far, these changes have not been successfully correlated with changes in the oil; for instance, it is known that folic acid decreases in stored fish meal to a marked degree, but this decrease takes place to an equal extent both in oily and hexane-extracted fish meals.

The effects of fish oils in meals can therefore be considered to be very complex and difficult to measure. As fish meals age, the amount of hexane-extractable oil decreases rapidly. The same decrease in ethyl ether extractables is noted, but after a much longer period of time. Preliminary investigation indicates that, with time, the oil in some manner becomes attached to the non-fat portion of the meal, probably the protein, and that this process follows a preliminary oxidation of the oil. Prevention of the oxidation of fish oils in meals and/or rations is therefore necessary for maximum stability of the complete ration. With the very large potential market for fats in feeds and with the undeniable physical advantages that liquid fish oils possess over solid high-melting fats, the solution to the problem of stabilizing fish oils in feeds would certainly do much to promote their wider use in this field.

III. Industrial Uses

Fish oils find their greatest use in industry, either unmodified or after pre-treatment. The fish body oils such as menhaden, herring and sardine, are the so-called 'drying fish oils' and considerable quantities of these find their way into various specialized coatings. Soaps consume some fish oils, either with or without modification and the less unsaturated fish liver oils are used in leather manufacture, usually after sulphonation. Oil-tanned leathers, on the other hand, are made with untreated fish oils. A variety of small miscellaneous uses of fish oils have been developed and these for the most part depend on the unsaturated character of the oils.

A. Protective coatings

The fish body oils, as mentioned above, will dry and eventually form a solid film. A comprehensive study of the characteristics of fish oil films was made some years ago by Denstedt and Brocklesby (1936). Since an understanding of the defects of fish oil films is necessary before some modern processes can be evaluated a summary of the above work is pertinent.

The formation of a solid film from a drying oil proceeds in four main stages: a period of induction, micelle formation, gel formation and finally the setting of the gel to form a solid. The first three stages may be accomplished without oxygen, but the final stage definitely requires oxygen. The type of film finally produced depends on the nature of the unsaturated bonds in the oil and also to a great extent on the nature and amount of non-drying components (such as saturated fatty acids). Since oxidation occurs more rapidly at the exposed surface and since the formation of cross linkages is associated with oxidation, it is obvious that solidification begins at the surface and proceeds inwards. At the same time, the non-drying components are squeezed inwards also. Microscopic examination of fish oil films under crossed nicols reveals spherical crystalline masses of varying diameter imbedded in the lower layer of fish oil films. These masses have not been detected in linseed oil films. Extraction of dry fish oil films with absolute ethyl alcohol yields a white crystalline material.

Analysis reveals this to be a mixture of saturated glycerides and solid fatty acids. The bulk of the material melts between 55 and 57°C. but a small portion melts at about 80°C.

The effect of these non-drying components on the properties of fish oil films was shown by the above authors by the use of a modified polymerization process. The fish oil was polymerized by superheated steam at 300°C. A 60 per cent yield of an elastic rubbery gel was obtained. The distillate consisted largely of saturated fatty acids together with aldehydic and ketonic decomposition products. The gel, which acted as an extremely viscous fluid, would dry very rapidly to yield a very tough and hard film. Only a trace of crystalline solids could be detected on microscopic examination, but the improvement in physical properties was very marked.

In general, fish oil films, made either from raw or winterized oils, are soft and tacky. They are more permeable to moisture than those of linseed oil films and have a pronounced tendency to become dull and to bloom. These defects can be almost entirely overcome by the steam polymerization process mentioned above. Partial improvement can be effected by the judicious use of driers, a mixture of cobalt and cerium giving the hardest films. Pretreatment of the oil with sulphur dioxide gas was found to increase the rate of drying and to improve the hardness of the film. However, this treatment reduced the durability by about one third. Oven drying and baking was found to have a definite effect, the films being harder, and more resistant to moisture. However, there is little removal of the saturated components during baking, and these are squeezed more compactly into the lower layer of the film. The result is that after a period of time these solid components will migrate to the surface again and cause a bloom.

It became quite apparent during the above study that the most important factor determining film properties was the proportion of solid non-drying components. If these are removed then very satisfactory films can be produced from fish oils notwithstanding the differences in structure of some of the highly unsaturated fatty acids from those in vegetable oils.

Swain (1952) removed varying proportions of stearine from pilchard oil and then determined the amount of saturated fatty acids left in the clear oil and followed this with an investigation of the hardness of films of the various oils after drying in the presence of a cobalt drier. The data obtained will be found in Tables 23 and 24 of Chapter 5. It will be noted that the removal of 22 per cent stearine effected a reduction of but 2·4 per cent of saturated fatty acids. In spite of this, however, the hardness of the dried films was materially improved. It is obvious that the stearine must consist of a variety of mixed triglycerides, made up of about 1 part of saturated fatty acids to 9 of unsaturated. Cold clearing of fish oils is thus a very inefficient method of removing saturated fatty acids or glycerides. Improved processes have been devised to separate the saturated fatty acids from the unsaturated, some in the form of glycerides, some as esters of monohydric alcohols and some as the free fatty acids. A few examples will be described.

B. Segregation of glycerides

One of the most interesting processes for the removal of saturated glycerides from fish oils is Eckey's directed inter-esterification process. If a liquid mixture of a glyceride and an alkaline catalyst is gradually cooled, the least soluble portion will gradually crystallize from the mixture. As the solid components are removed from the reaction mixture, the equilibrium is disturbed and more saturated glycerides will be formed as the system tends to produce an even distribution of the various fatty acids in the mixed glycerides. By proper selection of the temperature conditions, it is thus possible to bring about rearrangement of the glycerides with accompanying removal of the trisaturated components. Eckey applied this method to menhaden oil as follows: The oil (iodine value 177, total saturated fatty acids 24·5 per cent) was first blown with steam under a vacuum for 30 min at 350°F. It was then cooled to 120°F and mixed with 0·2 per cent sodium methoxide and then cooled quickly to 85°F. It was then seeded with a small amount of slurry from a cottonseed oil segregation run, slowly stirred in an airtight container for 20 h at 80°F, 26 h at 70°F, and finally 96 h at 60°F. After inactivation of the catalyst the oil was subjected to crystallization from petroleum ether at 20°F when a yield of 21·9 per cent of crystals was obtained with an iodine number of 4·6. When crystallized from petroleum ether under identical conditions the original menhaden oil yielded only 1·1 per cent of saturated crystals. Thus almost the entire amount of saturated fatty acids were rearranged into saturated glycerides. (Eckey, 1948a,b)

The increased percentage of saturated glycerides resulting from this directed inter-esterification means a more complete removal of such glycerides from the liquid fish oils is now possible either by the use of conventional 'cold-clearing' methods or by the more efficient solvent segregation processes, such as the liquid propane (Solexol) and furfural methods. Passino (1949) has given a detailed account of the Solexol process with examples of menhaden and sardine oil treatment. To the writer's knowledge there are no available data on the application of the Solexol process to a rearranged oil. However, when one considers what the process will do to raw oils it is easy to visualize what it will do to oils whose total saturated fatty acids are combined as saturated glycerides. Treatment of menhaden oil with a propane counter-current extraction in a three-tower system resulted in four fractions. A 2 per cent bottoms fraction containing most of the colour bodies was first removed, followed successively by a 20 per cent high iodine fraction, a 68 per cent intermediate iodine value fraction and a 10 per cent low iodine value fraction. The iodine value of the original oil was 175, of the high iodine value fraction 225, of the intermediate fraction 165 and of the low iodine fraction 90. A sardine oil with an iodine value of 185 was fractionated into groups with iodine values of 240, 160 and 110. This represents a considerable degree of fractionation and probably about the maximum that is commercially feasible. A limiting factor, of course, is the almost complete distribution of the saturated fatty acids among all the different

triglycerides as shown in Table 21 of Chapter 5. It would be very instructive to combine the Eckey process with the Solexol or furfural process, as fish oils free of saturated fatty acids would certainly be of greater value in the protective coating industry than those presently produced.

Before leaving this subject of fractionation, mention must be made of a process that has had some commercial success. By extracting a partially polymerized oil, such as sardine, BEHR (1939, 1941) succeeded in obtaining a drying oil tolerably free from saturated fatty acids. The extracted polymerized oil has but little tendency to throw down a 'polymer cloud'—a tendency that is very pronounced when raw or even cold-cleared fish oils are polymerized. The amount and rate of formation of the polymer cloud is directly related to the degree of polymerization. PRIVETT *et al.* (1947) studied the solvent segregation of heat-polymerized vegetable oils and concluded that polymerization proceeds according to the level of unsaturation; the most highly unsaturated are polymerized first, followed by the lesser unsaturated in order of decreasing unsaturation. These authors found that under specific polymerization conditions a high degree of selectivity can be achieved in solvent segregation to provide a series of oils with a wide range of properties.

The same selective reactions take place with fish oils during heat polymerization (BROCKLESBY and DENSTEDT, 1952) but in addition there is a progressive development of the so-called polymer cloud. This has proved to consist largely of saturated glycerides that become progressively less soluble as polymerization increases. The reaction is most probably an example of a directed ester interchange. The temperature of polymerization is sufficiently high to allow of the interchange of fatty acids: the directing effect is the result of (1) the lowered solubility of the saturated glycerides in the polymers or perhaps (2) to some steric hindrance which prevents the reattachment of saturated fatty acids to polymerized glycerides. It would appear that solvent segregation of properly polymerized fish oils is a sound procedure to improve the drying properties of such oils.

The processes of distillation and crystallization have been more widely adapted to the separation of the component fatty acids of fats and oils than have the liquid extraction processes described previously (MUCKERHEIDE, 1954). The reason for this is that a much more efficient separation is obtained with free fatty acids or with simple esters than is possible with non-rearranged mixed glycerides. With the development and perfection of continuous column vacuum stills it is now commercially feasible to separate naturally occurring mixtures of fatty acids into groups based on the chain length of the molecules. From such processes there are now available both saturated and unsaturated cuts of fish oils. Two examples of the latter may be mentioned. In one, the iodine value averages about 190, acid value 100; the composition is stated to be a mixture of polymerized glycerides and fatty acids of the C_{20} and C_{22} unsaturated series. Obviously, this fraction is a residual fraction. It has a dark colour and 2·5 per cent unsaponifiable matter. The other cut has an iodine value of 235 and a neutralization value of 184. It is pale yellow with an

unsaponifiable matter per cent of 0·5. It consists of about 90 per cent unsaturated C_{20} acids with about 10 per cent monoenoic and dienoic acid of the C_{18} series. This is a distilled fraction and is probably the most highly unsaturated fatty acid mixture commercially available.

One of the better known crystallization processes for the separation of fatty acids is the Emersol process (Muckerheide, 1954) which involves the controlled crystallization of the fatty acids from a chilled polar solvent, the crystallized acids being continuously removed by filtration. Using this process, sardine oil fatty acids, with an iodine value of 160 and a saturated fatty acid content of about 30 per cent, was separated into a solid fraction, yield 25 per cent and iodine value of 30, plus a liquid fraction which had an iodine value of 201 in a yield of 75 per cent.

From a protective coating standpoint, the above segregation processes can be looked upon as means for upgrading fish oils. Other methods for upgrading drying oils have come into prominence in the past few years, including copolymerization and esterification with polyols containing from 4 to 6 hydroxyl groups. The use of such treated oils will be considered along with fish oils processed by more conventional methods. Cold-pressed fish oils with or without alkali refining are used in alkyd resins, stack and other heat-resisting formulations, rustproofing and impregnating compounds. They are also used to some extent in the manufacture of oilcloth and linoleum and in formulations intended for rough wood and concrete paints.

Cold-pressed fish oils are generally used in oil blends with perilla or linseed oils. Such blends tend to reduce the shortcomings of straight fish oils referred to earlier. In short oil varnishes the addition of fish oils improves elasticity and increases compatibility with pigments (Carrick, 1950).

Blown fish oils are available in various viscosities. They are usually produced from cold-cleared oils. Their main uses are in flat paints, outdoor industrial paints and printing inks. On the other hand semi-gloss and high-gloss enamels can be made from polymerized fish oils. These are usually heat-polymerized in a vacuum to improve colour and maintain low acidity. They are available in a large range of viscosities. Sardine oil is also available in a polymerized–blown form. In this case the oil is given a preliminary polymerization to medium viscosity and then blown with air to viscosities ranging from 90 to 150 poises. It is then cut back with thinner to yield a product which retains the brushing and levelling characteristics of blown oils.

Considerable care has to be exercised in all these treatments of fish oils, otherwise the considerable amount of stearine present even in cold-cleared oils will precipitate out as a polymer cloud. It may be mentioned, however, that the tendency for this cloud to form is less in blown oils than in the polymerized oils.

The process of copolymerization is a comparatively recent development of great importance in upgrading of drying oils. An excellent review has recently been presented by Hovey (1950), and this paper should be consulted for practical details of the process.

The process actually involves the addition of small monomeric units to the unsaturated bonds in the drying oils. The two most important monomers at present in use are styrene and *cyclo*pentadiene. In the case of styrene it is usual to use a catalyst such as benzoyl peroxide or boron trifluoride. Preliminary blowing of the oil is also of advantage since the peroxides catalyse the copolymerization. The equipment used for styrenation consists essentially of that used for the azeotropic preparation of alkyds.

Copolymerization with *cyclo*pentadiene must be carried out in an agitated high-pressure stainless steel autoclave. Since *cyclo*pentadiene polymerizes very rapidly to the dimer, the latter is used as a source of the monomer. The di-*cyclo*pentadiene is mixed with the oil and carefully heated. The *cyclo*pentadiene gas reacts with the oil rather than re-forming the dimer. The reaction proceeds with a very small amount of catalyst and will even take place without any catalyst.

The advantages of copolymerized oils are the increased hardness, greater drying speed and better water and alkali resistance. Fish oil copolymers form elastic polymers, light in colour, free from after tack (a remarkable improvement over the raw oils) and are rapid drying (Hovey, 1950). One large company in the United States makes a series of five *cyclo*pentadiene copolymers of fish oil which they recommend for the following uses: exterior paints, decorative interior flats, non-penetrating flats, primer–sealers, semi-gloss finishes, high-lustre finishes, deep-tone flats, stipple finishes and for alkyd monoglycerides. This represents a much wider use of fish oils in the protective coating field than is possible with the natural oils—a situation that is all the more remarkable when it is considered that these copolymers are made from whole fish oil.

Another upgraded oil is represented by the reaction product between fish oil and maleic anhydride and glycerine. This product is classified as an alkyd, which, to the paint industry, means an oil-modified polyol ester of a dibasic acid. Refined fish oils are used in the manufacture of these maleic acid reaction products and the producers recommend them for use as a kettling oil or for replacing Chinawood oil. These products are valuable in floor and spar varnishes.

A number of polyhydric alcohols with a functionality greater than glycerol are now being used in the preparation of protective coating intermediates. These include pentaerythritol, polypentaerythritol, sorbitol, tetramethylol-*cyclo*hexanol and inositol. Improvements in the drying or bodying rates of drying oils may be obtained by replacing the glyceryl radical with one of these polyols or, preferably, by a combination of these polyols. Esterification is usually effected by heating the free fatty acids of the oil with the mixed polyols for specific times and temperatures depending on the type of fatty acids and the polyol mixture. The reaction is carried out under an inert atmosphere until the acidity is reduced to the desired level. Due to the highly unsaturated nature of fish oil fatty acids great care has to be taken not to polymerize these acids during the esterification. This is usually accomplished by the proper selection of the polyol mixture, some polyols esterifying more rapidly than others. From the information available, fish oils modified in this manner have

improved drying characteristics but the improvement is not so marked as in the case of the copolymerized oils.

Fish oils are used to a certain extent in the production of oleoresinous varnishes (HAFELI, 1950). This author states 'Great strides have been made along the lines of chemically processing fish oils and more of the treated oils are being accepted each year. One of the outstanding disadvantages of any form of fish oil has been the characteristic odour which is inherent in this oil. Fortunately, this odour has been the object of determined study by the oil companies, and we are now entering an era when odourless fish oils for use in varnish are a distinct factor.'

Drying oils are used in large quantities in the manufacture of printed felt base floor covering and in linoleum. Felt base floor coverings are essentially an asphalt saturated felt on which is applied a decorative baked enamel surface coating. In order to seal the asphalt and to provide a suitable surface for the enamel top coat, a coating paint must first be applied to the saturated felt (O'HARE, 1950; FISHERIES RESEARCH BOARD OF CANADA, 1952). This coating paint must have good film-forming properties that will give a good seal over the asphalt and yet retain flexibility. This latter property is of great importance. The chief oils used in these coating paints are linseed, soybean, fish, tung and oiticica. The fish oil is usually cold-cleared and it is used in combination with one or more of the other oils listed, usually linseed.

Linoleum is made by applying a thick layer of 'cement' to a woven or felted fabric backing. The cement consists of oxidized drying oils and resins mixed with cork or wood flour, mineral fillers and pigments. The oxidized drying oil is made by various methods, but essentially consists in a carefully controlled air blowing process, during which time the oils are stirred with powerful paddles. Resins are either added during the blowing or may be fluxed into the heated oxidized oils (*Encyclopedia of Chemical Technology*, 1952). The oxidized mixture is then poured into thick slabs and allowed to cool and age.

O'HARE (*loc. cit.*) has defined the characteristics of the oxidized oil or 'cement' as follows: 'In the production of cement it is essential that the oil be readily oxidizable since the cement must be in a highly oxidized state to attain the desired binding qualities. This is also necessary since the seasoning of the linoleum sheet is essentially a polymerization of the oxidized binder. The time and nature of the seasoning, then, will be greatly dependent on the nature of this binder. This cement must lend itself readily to efficient mixing with the pigments and fillers: for this reason it must have good wetting properties. The mix formed from the cement pigments and fillers is a soft plastic mass. The sheet formed from this mix must be able to support its own weight during processing so that it must have good tensile strength.'

Blown fish oils have many of the desirable characteristics listed above, including excellent wetting properties. However, a non-segregated fish oil, even after cold-clearing, tends to produce a 'short' rubbery gel. For this reason fish oils must be combined with linseed or soybean oils to produce the most desirable linoleum cements.

Other uses of fish oils in which their drying properties are utilized include the manufacture of oilcloth, waterproof fabrics, printing inks and core oils. In the printing ink field heat-bodied linseed oil still predominates over all other oils. However, in recent years considerable interest has been shown in *cyclo*pentadiene copolymerized fish oils. These oils heat-body very well, dry fast and hard and have excellent resin compatibility. Their outstanding defect is poor pigment wetting ability and dispersion characteristics. If these defects can be overcome then such oils may increase in printing ink production.

Core oils are used as a binder for sand in forming the mould in which metal castings are made. The core oil should reach a maximum strength in 3 or 4 h at 425°F. The mould should be porous, with sharp edges and should readily disintegrate after the casting has been poured. Experiments with fish oils (Fisheries Research Board of Canada, 1941) as core oils showed that tensile and transverse strengths of the baked moulds were never as great as those made with linseed oil as the core oil. However, in practical tests, fish oil core oils were judged to be as satisfactory as linseed or commercial core oils.

Finally, drying fish oils find uses in a number of miscellaneous products such as caulking compounds, glazing compounds, rustproofing formulæ and stamping and drawing compounds. A good account of these uses will be found in a paper by Gutkin (1950), who points out the specific properties of the oils that make them particularly desirable in the above products.

C. Non-drying uses of fish oils

The commercial use of fish oils in the non-drying field is chiefly in the use of the completely hydrogenated fats or hydrogenated fatty acids. The latter have the greater use.

The cosmetic industry is a large user of single-, double- and triple-pressed stearic acid. Its use is either as the acid or as salts, zinc stearate being in greatest demand. So far, hydrogenated fish oil fatty acids have had but little acceptance by the cosmetic industry. The specifications for stearic acid are rigid, particularly with respect to odour and stability against rancidity. In these respects hydrogenated fish oil fatty acids have not as yet been able to compete economically with stearic acid. Undoubtedly, from a technical standpoint, good stability in the hydrogenated fish oil fatty acids can be attained, but it is difficult to accomplish and this places an economic barrier on its use in the cosmetic field. One of the drawbacks to hydrogenated fish oil fatty acids is the presence of traces of *iso*-acids which reduce the oxidative stability and contribute to the lingering hydrogenation odour.

In commercial fields where such rigid restrictions are not necessary, hydrogenated fish oil fatty acids are used in considerable quantities in the rubber industry, in the manufacture of lubricating greases, metallic soaps, buffing compounds, wax compositions and the like. For these purposes the hydrogenated fish oil fatty acids with iodine values ranging from 2 – 10, unsaponifiables about 0·5 per cent and acid value 192 to 197 are commercially available. Partially hydrogenated fish oils are also produced for soap making.

The chief function of stearic or solid fatty acids in rubber curing is probably a chemical one. Practically all accelerators used during vulcanization contain zinc oxide which is insoluble in the rubber mix. Natural rubbers contain varying amounts of stearic acid, and in order to standardize the process the content of fatty acids must also be standardized. The role of these acids is to dissolve the zinc oxide and also to act as a softener and plasticizer. Stearic acid is not unique in this field, other saturated fatty acids being just as effective. Unsaturated acids will also function in the above role but are deleterious in that they cause a bloom to appear in the finsished rubber and produce a rubber with inferior physical properties. Fish oil hydrogenated fatty acids with low iodine values have found wide acceptance in the rubber industry, particularly in the manufacture of tyres and moulded mechanical goods.

Nearly all lubricating greases made today contain soap as a thickening agent. These soaps are chiefly calcium, sodium, lithium, aluminium and barium salts of tallow or hydrogenated tallow fatty acids. The fatty acids of hydrogenated soybean, cotton and fish oils are also used in considerable quantities. Although price is certainly an important factor in the choice of fatty acid used, physical and chemical properties are also of importance. Chief among these is stability against oxidative changes, and this is a field in which considerable attention has been given by grease manufacturers as it has enabled them to produce greases that can be factory pre-packed in anti-friction bearings. In addition to the stability factor, actual physical properties of the soaps of the fatty acids used is of very great importance. Most grease manufacturers have, by experience, learned which combinations of fatty acids give them the best results. What they are now concerned with is uniformity of raw materials. Since there is less variation in chemically refined products than in natural fats or oils, the tendency is towards the former class of goods. Hydrogenated fish oil fatty acids should therefore continue to enjoy increasing use provided that factors of stability and uniformity are emphasized.

Whale and fish oils are used to a considerable extent in the manufacture of yellow laundry soaps, powered soaps, soap chips and cleansers. The use of raw fish oils is not acceptable due to the great tendency of the soap to go rancid. Furthermore, the large amount of highly unsaturated acids limits the upper temperature range of efficient use, because above 105°F the sodium soaps of these highly unsaturated acids go into true solution and lose their colloidal characteristics. Hydrogenation of fish oils increases detergency efficiency up to the point where the polyethylenic acids are reduced to monoethylenic. Beyond that point, where saturated acids are formed, hydrogenation reduces the detergent efficiency. For most fish oils reduction of the iodine value to between 70 and 80 gives an oil that will yield an excellent soap. Again we have the problem of *iso*-acid formation and that of stabilizing against oxidative rancidity. By careful selective hydrogenation, however, the amount of saturated acids formed in reducing the oil to an iodine value of 70 can be kept to a minimum as can also the *iso*-acids. For all practical purposes the use of a partially hydrogenated fish oil for use in laundry soaps, chips and cleansers is a matter of economics.

There are numerous minor uses of fish oils some of which depend on the specific structure of such oils. For example in oil tannage, used for the preparation of chamois, and other soft leathers the oxidation of the fish oil actually is an essential part of the tannage process. During the tannage process, the unsaturated fatty acids actually combine chemically with the collagen of the skins while the associated saturated fatty acids give a softening effect to the finished skin. For examples of other interesting but minor uses of fish oils the reader is referred to *Fisheries Research Board of Canada Bulletin* 89 (1952).

With the development of efficient commercial segregation processes, fractions of fatty acids of specific chain length and unsaturation will undoubtedly become available. The production of highly unsaturated alcohols has already been accomplished and the use of such fatty acid derivatives as chemical intermediates for the formation of synthetic drying compounds, detergents, emulsifiers, etc. holds much promise for the future.

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8

RECENT ADVANCES IN THE TECHNOLOGY OF DRYING OILS

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8

RECENT ADVANCES IN THE TECHNOLOGY OF DRYING OILS

Alfred E. Rheineck

1. Introduction

A. Influence of World War II on drying oil chemistry

The development of improved drying oils and protective-coating materials has been influenced by economic and social upheavals. The developments within the last 20 years have been largely the result of the pre-World War II era and the war itself. Wars always cause profound economic and technological changes. These changes are responsible for the availability of new raw materials for use with drying oils and as protective-coating products.

World War II can be considered a major factor responsible for freeing the protective coating industry of its dependence on China wood oil*.

Before the war, China wood oil was used extensively in oleoresinous varnish systems. Between 85 and 90 per cent of the China wood oil used for varnishes came from the inner areas of China. The amount of this oil obtained from young groves planted in other parts of the world was insignificant. Reduced imports because of the Sino-Japanese War and then World War II presented the basic problem of obtaining a product from domestic materials which would perform in a manner similar to China wood oil.

Prior to the middle 1930s, studies on drying oils were limited to investigating the changes that took place when an oil film dried and the reactions that took place during heat polymerization. The literature of this period indicates that chemists were more concerned with these changes than they were in making improvements in drying oils. However, a broader study of drying oils was initiated in the late 1930s when it was anticipated that the supply of China wood from the Orient would be discontinued. A considerable volume of research was undertaken to improve and modify oils not based on Asiatic sources (excluding perilla oil). This objective did not necessarily imply that the oils were to be chemically the same as China wood but rather that the end products, varnishes and enamels, were to have the same performance characteristics.

The change in the course of oil research was given a further impetus by the Japanese invasion of China, which reduced export of China wood oil from China.

* The term 'China wood oil' is used throughout this chapter in preference to 'tung oil'. The former has been accepted to mean the oil obtained from China, while the latter term is reserved for oil of non-Oriental origin.

Work on oil modification proceeded through the war period and fruits of such research have now become available for civilian use.

It was anticipated by some that as soon as shipping facilities readjusted in the post-war period China wood oil would again become available to world markets and probably be used at somewhere near the pre-war level. This anticipation was justified on the basis that about 20 per cent of the Chinese exports were in the form of China wood oil. However, the interest of varnish and oil chemists in China wood oil in the post-war period waned. In the first place chemists learned that they could successfully prepare products with the desired preformance characteristics without China wood oil. Secondly, the situation in China did not permit an assured delivery of large volumes of the oil. Finally, new chemical compounds developed during the war were becoming available for coating use. These included latex rubber systems; vinyl coatings and resins; acrylic-based latices and resins; epichlorohydrin–*bis*phenol resins such as the 'epons'*; olefinic hydrocarbons, e.g. *cyclo*pentadiene, butadiene and homologous dienes; vinyl aromatic compounds, e.g. styrene, vinyl toluene; polyesters†; and drying oils from petroleum sources. Increased production of maleic anhydride, phthalic anhydride, pentaerythritol, and synthetic glycerol are of varying importance, especially as related to polyesters and alkyd resins ‡.

B. Rationale of oil researches

The major problem facing drying oil chemists was to find a substitute for China wood oil. It was soon learned that there was no substitute, and other oils were then considered primarily as replacements. It is not known whether chemists consciously or instinctively followed certain functionality rules to produce modified oils. A careful study of the work which has been done indicates that there were several concepts related to the drying properties of the oils. They were that an isolated double bond has a functionality of 1, that conjugated double bonds have a functionality of about 50 per cent greater than the same number in isolated positions, that each hydroxyl group in a polyol has a functionality of 1, and that the average product of total hydroxyl functionality and the double bond functionality should be a minimum of 6. These concepts are based upon the measurement of certain properties of oil films, such as drying time, Sward Rocker Hardness, and other physical characteristics.

Thus, linseed oil fatty acids with an iodine value of 180 (the equivalent of 2 double bonds per acid chain) esterified with glycerol (functionality of 3) yields a product of 6. Similarly soybean fatty acids with an iodine value of 135 (the equivalent of $1\frac{1}{2}$ double bonds per acid) esterified with pentaerythritol (functionality of 4) yields a product of 6. The drying characteristics of the two oils are similar. This concept has some limitations in that it does not take into

* Epon Resins—Shell Chemical Corp.

† Polyesters are defined as the reaction product of a dibasic acid and a polyhydric alcohol *per se*, or polymerized with an olefinic hydrocarbon.

‡ Alkyd resins are defined as the reaction product of a dibasic acid (preferably phthalic) with a polyhydric alcohol and modified with fatty acids, either saturated or unsaturated.

account the effect of traces of impurities. Nevertheless, it has proved useful in the preparation of drying oils. Based upon these concepts, the oil modification work which was undertaken prior to the war can be summarized here. Change in fatty acid radicals was effected by the introduction of double bonds, either by dehydrogenation or dehydrohalogenation, and by shifting double bonds by isomerization. Introduction or substitution of polyols was accomplished by direct esterification or by ester interchange. Other developments indirectly related to or supplementing the foregoing, each of which will subsequently be discussed in detail, are summarized as follows. Reactions to increase molecular complexity include polymerization and separation of unpolymerized portions, copolymerization and building resinous characteristics into the molecules. Increase of unsaturation can be achieved by segregation of glycerides via solvent processes or inter-esterification processes. Segegration of acids is accomplished by crystallization, distillation or preferential esterification.

C. Availability of tall oil and oiticica oil

The period immediately before the war saw the introduction of tall oil and oiticica oil in quantities sufficient to interest large oil consumers. Both oils have been subjected to the same types of modification that were developed for and applied to other oils.

Because tall oil is a mixture of fatty and resinous acids, esterification by a polyol is necessary for use in coatings. In the years 1940–45, tall oil was subject to less wartime restrictions than drying oils in common use. This encouraged its use, but limited availability of pentaerythritol and glycerol prevented the widespread application attained in the post-war period. Today, tall oil enjoys a very enviable position. Because of its low price, the demand exceeds the supply. In 1943, 2 million lb were used in paints, coatings and resins, but, in 1953 the corresponding figure was 75 million lb (Archer-Daniels-Midland, unpublished.)

Oiticica oil was introduced as a China wood oil replacement, since it was thought to be chemically similar. However, varnish performance characteristics and chemical analysis, soon showed it to be different. Varnish films showed greater embrittlement and erosion by weathering than similar China wood oil varnish films under the same conditions. This weakness probably is due to the presence of the ketone group which Brown and Farmer (1935) demonstrated was present in the 4-position of the major constituent, licanic acid. (See Table 5.)

One factor, however, that tended to disfavour the acceptance of oiticica oil was its price. This was stabilized at a constant differential below the China wood oil market price in the pre-war era. If its performance characteristics had been more favourable, there would have been a good chance for its acceptance in spite of the rising China wood oil market. Supply was adequate because its source, Brazil, was not closed off by the war. Later, methods were found to overcome its inherent weaknesses in varnishes, but costs were unfavourable, and encouraged the use of other modified oils.

The acceptance of one type of modified and treated oil over another in the years 1940–45 was markedly influenced by cost, availability, and allocation of equipment and raw material for production.

D. Scope of material presented

The discussion which follows is limited to methods for improvement of oils. At one period or another all methods discussed were considered important, but relatively few have survived in the production of commercial products. Products that have survived are maleic anhydride-treated oils, dehydrated castor oils, copolymer-type oils (including di*cyclo*pentadiene and styrene modifications), and reconstituted oils (pentaerythritol type, etc.).

The discussion is further limited to the technology involved in modifying and improving the drying properties of oils. During this same period improvements were made in the methods of recovering and refining vegetable and fish oils, but these will not be considered. Discussions of these improvements will be found in other chapters of this volume.

II. Changes in Fatty Acid Radicals

A. Introduction of double bonds

1. *Dehydration of castor oil.*

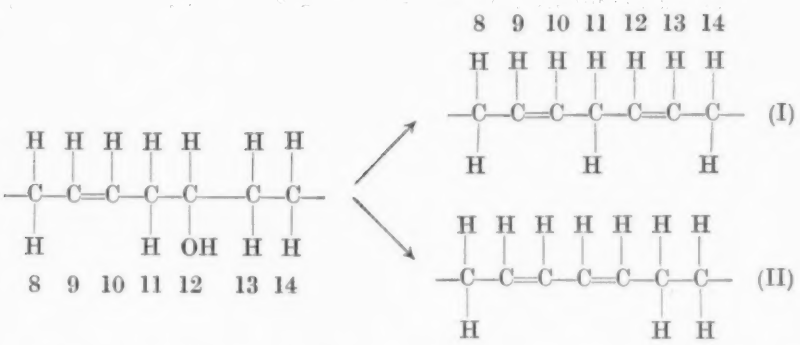
Historically, the dehydration of castor oil to a drying oil dates back to the early work of Krafft in 1877. This was followed in 1914 by the work of Fokin, who described a method in which phosphoric acid was used as a catalyst to dehydrate the oil. In later work by Scheiber in 1933 castor oil fatty acids were dehydrated to what he described as conjugated dienoic acids, and these were re-esterified with glycerol. Even following this, until about 1938, castor oil was not used as a source of drying oil; but was used mainly in lubricants, textile oils, plasticizers, and medicine.

Shortly after Scheiber's work, it became evident that a new source of a conjugated oil was needed because of the shortage of China wood oil. For this reason, chemists became more interested in improving processes for preparing dehydrated castor oil. Most of the work was undertaken in the years prior to 1945. A major portion of the patents issued for processes covering the dehydrated oil appeared in the years 1937–45. Since the latter date, few patents have been issued on any improvement of the preparation of the oil.

When castor oil is dehydrated there are two possible courses of reaction. These are illustrated by the mechanism shown on page 171.

A 9–12 non-conjugated system and a 9–11 conjugated system are both formed during the dehydration reactions. The catalysts that are generally used for dehydrating castor oil comprise a wide range of materials including mainly organic acids, inorganic acids, acid salts, anhydrides and naturally occurring acidic earths. They are listed in Tables 1 and 2.

The methods for preparing dehydrated castor oils include (a) **preparation of dehydrated acids** (Scheiber Process) followed by re-esterification with a polyol,



(b) the **catalytic method** in which the amount of catalyst is in the range of ·01 per cent to 5 per cent of the oil weight, and (c) the **chemical method** in which stoichiometric quantities of acids and castor oil are reacted to form secondary esters, which are then pyrolyzed.

All three processes have been used commercially. Oils made according to the patents of SCHWARCMAN (1939, 1942), UFER (1932), AUER (1943), BROD (1941), COLBETH (1942, 1943), and RHEINECK and CRECELIUS (1941, 1944a) were used in the United States. These appeared under various trade names as Synthenol, Kast-o-lene, Castung, Isolene, Dehydrol, and PGD oil.

The 'Scheiber oil' was known in Germany as Synourin. Deinol, Pythrinol and Veorin, are the Swiss, French and Dutch oils (VON MIKUSCH, 1949).

(a) *Scheiber process oils.* SCHEIBER (1928, 1933, 1934) originally claimed that the product predominating in his dehydrated oil was conjugated to the extent of about 90 per cent, but at the time of his work there was no good quantitative method for the measurement of conjugation. Performance properties of the oil as such and in varnishes, indicated that this high concentration of conjugated material could not be present, and the actual amount of conjugation was soon demonstrated conclusively to be lower than claimed by SCHEIBER.

In 1936 methods for measuring diene conjugation were announced independently by KAUFMANN and BALTES (1936) and by ELLIS and JONES (1936). These so called 'diene value' procedures when applied to dehydrated castor oil and its acids indicated that there was not over 25 per cent diene conjugation in a catalytically dehydrated oil. In a paper by PRIEST and VON MIKUSCH (1940) analyses are given for a variety of oils prepared under different conditions including one which was made by the Scheiber process in Germany. These analyses indicate that the highest percentage conjugation obtained was 29·6 per cent. SCHEIBER in 1949 claimed that ricinoleic acid dehydrated and re-esterified with glycerol produced an oil which contained about 70 per cent of conjugation.

(b) *Catalytic process oils.* Table 1 lists the catalysts that are used either batchwise or continuously in this process. The dehydration of the oil usually requires a temperature of about 240°C with small quantities of catalysts. Although it is not required, a vacuum is preferred to remove the water and

volatile decomposition products. The course of the dehydration reaction with catalysts can be followed by several methods:

(i) As dehydration proceeds the refractive index increases. A refined grade of castor oil has a refractive index of 1·4771 while a commercially available dehydrated oil has a refractive index of 1·4820–1·4840 at 25°C. The relationship between the degree of dehydration and refractive index does not hold for oils treated with acidic earths. The refractive index in this case increases for some unknown reason not related to dehydration and would therefore give an erroneous measure of the dehydration taking place.

(ii) Viscosity measurements on the oil during the dehydration also serve to determine the degree of completeness of the dehydration reaction. Fig. 1

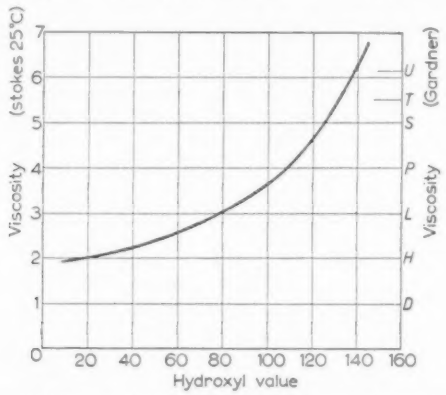


Fig. 1. Relationship between viscosity and hydroxyl value during the dehydration of castor oil according to SUNDERLAND and ANDREWS (1949).

shows the relationship between viscosity and hydroxyl values as determined from data given by SUNDERLAND and ANDREWS (1949).

(iii) Castor oil is miscible with ethanol. Upon dehydration of the oil the solubility in, and tolerance for, ethanol diminishes. Hence this property may be used in following the dehydration reaction.

Of the catalysts used to prepare commercial quantities of this oil, it is difficult to pick out any one which shows an advantage over another. The most widely used catalysts for the preparation of commercial quantities of the oil have been sulphuric and phosphoric acids, used as such, or in conjunction with a carrier, e.g. diatomaceous earth. The phosphoric-acid process is said to produce a slightly better-coloured oil than the sulphuric acid process. CARTER and BRISTON (1952) claim unusually light colours with *ortho*-phosphorous acid. Of the catalysts shown in Table 1, the most efficient for completely stripping the hydroxyl groups from the oil is tungstic acid, when prepared as described by RHEINECK and CRECELIUS (1941). This catalyst produces an oil with the lowest viscosity and the lowest hydroxyl values of any of those examined.

Generally, catalytically dehydrated oils are of low viscosity, in the range of 1–2·5 stokes. However, in a process described by RHEINECK and CRECELIUS

Table 1. *Catalysts for dehydration of castor oil*

Catalyst	*Remarks*	*Reference*
Sulphuric acid		Schwarcman (1942)
Sulphuric acid	On carrier	Schwarcman (1939)
Sulphuric acid	In thin layers	Colbeth (1946)
Sulphuric acid	Oil emulsion	Moser (1953)
Sulphuric acid	Continuous Process	Radlove (1950)
Sod. bisulphate		Ufer (1932)
Sod. bisulphate	With diallyl phthalate	Bent and Ryan (1944, 1946)
Sod. bisulphate	With polar compounds	Auer (1943)
Sod. bisulphate		Ivanova and Bespalko (1949)
Sod. bisulphate	Aqueous sol.	Münzel (1939)
Sod. bisulphate		Sivsamban *et al.* (1953)
Pot. pyrosulphate		Priester (1943)
Camphor sulphonic acid		—
Methionic acids		Priester (1940, 1941)
Alkyl sulphates		Schmutzler (1952)
Aryl sulphonates		Dole (1953), Dole and Keskar (1954)
Aryl sulphonates		Toyama and Iwamoto (1953)
Naphthol sulphonic acid		Walton *et al.* (1947)
Pyrosulphuric acid		van der Lande (1938, 1939a, b, c)
Polysulphonic acid		van der Lande (1938, 1939d)
Sulphur dioxide	Used as gas	Dussellier (1947) Estab. Robbe Frères (1949)
Phosphoric acid	Aryl esters	Ufer (1932)
Phosphoric acid		Fokin (1914)
Phosphoric acid	On carrier	Carter and Briston (1952)
Phosphoric acid	On carrier	Bloch (1945)
Phosphoric acid	With other acids	Priester (1940)
Alkyl phosphates		Gilbert (1944)
Phosphorous acid	With sulphuric	Carter and Jarvis (1952)
Phosphorous pentoxide		Bloch (1945)
Phosphorous pentoxide	With Mg sulphate	Sørensen (1941)
Phosphorous oxychloride		Schwarcman (1943b)
Phosphorous pentachloride		Schwarcman (1943b)
Aluminium phosphate	With steam	van Bockel (1944)
Molybdenum oxide		Münzel (1938a, b)
Tungstic acid		Rheineck and Crecelius (1941)
Tungstic oxide		Münzel (1938a, b)
Silico-, phospho-, borotungstic acids		Rheineck and Crecelius (1944a)
Aluminium Tungstate		Miller (1944, 1947)
Boric acid	Adduct with oil	Colbeth (1942)
Borax	With sulphuric acid	Colbeth (1942)
Borax	Forms oil complex	Colbeth (1943)
Boron phosphate		Rust (1948)
Misc. acids	Aqueous under pressure	Monroe and Ipatieff (1948)
Cationic resins		Grummit and Marsh (1953)
Maleic anhydride	With sod. sulphate	Ivanova and Bespalko (1949)
Maleic anhydride	As oil adduct	Grummit and Marsh (1953)
Alkaline earth chlorides		Bertaut and Kahneman (1951)

Table 1—*continued*

Catalyst	*Remarks*	*Reference*
Misc. oxides		Hole and Leather Cloth Co. (1944)
Misc. salts	Sulphates, chlorides	Rizzi (1939, 1942)
Lead oxide, white lead		Agster and Terrill (1949)
Pot. hydroxide	Aqueous-pressure	Kirschenbauer (1945a)
Pot. carbonate		Jaki (1937)
Zinc soaps	With phenol sulphonate	Morgan (1943)
Earths	Aluminium hydrate	Paluszek (1946)
Bleaching earths		Knöffler (1936)
Clays		Ufer (1928, 1929)
Bauxite		Ufer (1928, 1929)
Al. powder		Vigdorov (1945)
Kaolin	With sulphuric acid	Tsuchiya and Ohkubo (1952)

(1944a), catalysts such as silico-tungstic, boro-tungstic and phospho-tungstic acids serve a dual function in that they also act as bodying catalysts.

There are several continuous processes which involve passing the oil over a catalyst. Block (1945) used phosphoric acid on a silicious adsorbent.

The use of sulphuric acid mixed with oil cascaded over a hot surface is disclosed by Radlove (1950). Use of heated tubes (Société Rhodiaceta, 1953) is also mentioned. Sunderland and Andrews (1949) have described special equipment for the process.

Several papers review the history and properties of dehydrated castor oil and the merits of the various catalysts (Balbi, 1953b; Dole and Keskar, 1954; Neto, 1946; Prakash *et al.*, 1949; Scheifele, 1951; Terrill, 1953).

Table 2. *Chemical method for dehydrating castor oil*

Acidic Reagent	*Reference*
18 Carbon acid	Nessler (1943)
Neofat 19	Walton and Jordan (1943)
Rosin	Rheineck and Crecelius (1946)
Acetic acid	Grummitt and Fleming (1945)
Phthalic	Ubben and Price (1941, 1945)
Acetic anhydride	Nessler and Schuelke (1945)
Acetic anhydride	Brod (1941)
Naphthenic	Steick (1937)
Phthalic	Farmer (1937)
Polyacids	Saunders (1938)
Mono acids	Brunner and Lilly (1945)
Oleic acid	Chemische Fabrik Florsheim (1925)
Phthalic	Blümer (1937)
Mixed	Blümer (1941)

FORBES and NEVILLE (1940) studied the reactions with thirty-eight different catalysts and discussed the merits of each. They concluded that the mechanism of the reaction in the catalytic method is probably one of esterification of the hydroxyl group with the acidic catalyst, followed by pyrolysis, which simultaneously dehydrates the oil and regenerates the catalyst.

(c) *Chemical method.* The chemical method for the dehydration of castor oil involves complete esterification of the secondary hydroxyl group with any of a variety of acids, (cf. Table 2) followed by pyrolysis. The esters are easily formed by heating the oil with the respective acids through a temperature range from about 240 to 300°C where pyrolysis starts regenerating the original acid

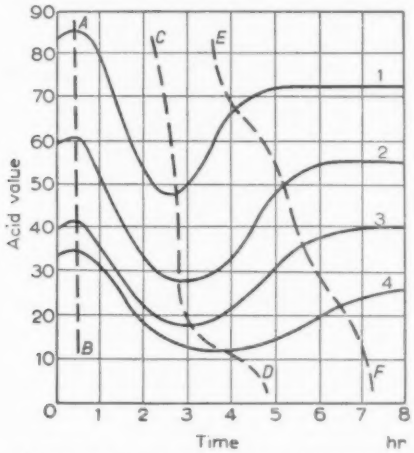


Fig. 2. Dehydration of castor oil by rosin (RHEINECK and CRECELIUS, 1946). Area ABDC—Esterification cycle; CDFE—Pyrolysis cycle; line AB—Maximum acidity resulting from loss of inherent volatiles; Curve 1—12½ gal varnish; 2—22 gal; 3—40 gal; 4—50 gal.

and the dehydrated castor oil. The liberated acids can either be removed from the oil by distillation under vacuum or they can be left in the oil and subsequently esterified. The use of C_{18} fatty acids in this process is of commercial importance.

In a process described by RHEINECK and CRECELIUS (1946), rosin acids are used to esterify the oil. The rosin acids remain in the oil after pyrolysis. Fig. 2 shows typical reaction curves for the dehydration step. Esterification of the acid by various polyols gives varnishes ranging from 12 to 50 gal.

None of the processes described up to this point has achieved the goal of complete dehydration to the conjugated isomer alone, i.e., 80–85 per cent, 9–11 octadecadienoic acid. Other than the re-esterified oil mentioned by SCHEIBER (1949), the highest yield of diene conjugated acids has been reported as 52 per cent by GRUMMITT and MARSH (1953). The latter oil was prepared by using alumina catalyst. As an explanation of this high conjugated diene content, they suggested that the alumina isomerized the oil during dehydration. The constants for this oil are compared with a commercial dehydrated oil in Table 3.

Table 3. *Comparison of properties of dehydrated castor oils**

	Alumina catalysed	*Synthenol*†
% diene conjugation	52	26
Iodine value (total)	183	156
Acetyl no.	5	28
Acid no.	10·6	4·8
Viscosity (Stokes, 25°C)	1·1	1·8
n_D^{25}	1·4868	1·4820
Colour (Gardner–Holdt)	10	5
Dry to touch	30 min	120 min

* According to GRUMMITT and MARSH (1953).
† Spencer Kellogg's.

(d) *Properties and uses.* Dehydrated castor oil behaves very similarly to China wood oil in many ways. Like China wood oil, the unbodied oil without drier gives a frosted film but the bodied oil with driers produces a clear, smooth, gas-proof film. When China wood oil and dehydrated castor oil are heat-bodied their refractive indices drop. This constant increases when soybean and linseed oils are bodied.

The drying properties of the oil lie between those of China wood and linseed oils. This is to be expected when the physical and chemical constants of these oils are compared (cf. Table 4).

Table 4. *Fatty acid composition of drying oils*
(ARCHER-DANIELS-MIDLAND)

Acid	*Castor*	*Dehydrated castor*	*Linseed*	*Oiticica*	*Perilla*	*Safflower*	*Soybean*	*Sunflower*	*China wood*	*Tall oil* fatty acids*
Myristic						0·1	0·1			
Palmitic	2	2	5·5	7	7	4·5	8·0	4·0	4	7
Stearic	1	1	4·0	5		2·0	4·0	3·0	1	
Arachidic			0·3			0·4	0·6	0·6		
Lignoceric			0·2					0·4		
Myristoleic							0·1			
Palmitoleic							0·2			1
Oleic	7	7	22	6	8	20	28	33	8	44
Ricinoleic	87									
Linoleic (9–12)		57	17		38	70	54	59	4	37
Linoleic (9–11)		30								11
Linolenic		3·0	51		47	3	5		3	
Eleostearic									80	
Licanic				78						
Others	3			4						

* Tall oil: Fatty acids 45%, Rosin acids, 42% Unsaponifiable 13%.

Although dehydrated castor oil was originally regarded as a substitute for China wood oil it is not being used as such at the present time. Because it will dry rapidly and form films with a high degree of flexibility, durability and pale

colour it has found use in a great many products where no other natural oils serve the purpose. It has found a place of its own in the protective-coating field, especially in alkyd resins where freedom from yellowing is desired.

Dehydrated castor oil has one undesirable property in film formation, a development of an after-tack which appears in 5–12 days after a film has apparently dried completely. LILLEY and CARTER (1952) and WILSON (1948) reviewed the problem of after-tack. It was suggested that the effect might be caused by the presence of decomposition products, or by undehydrated oil and dihydroxystearic acid, or by oxidation products released within the film during drying, which were derived from certain of the geometric structures in the dehydrated product. It was also suggested that the phenomenon might be related to the degree of conjugation, but LILLEY and CARTER have shown that this is not the case. They feel that a relationship exists between molecular size and degree of after-tack.

WILSON (1950) made the following recommendations to eliminate the after-tack: incorporation of a small quantity of ethyl cellulose with the oil; re-esterification of the fatty acids derived from the oil with an alcohol more functional than glycerol; maleic modification of the oil followed by esterification with a polyhydric alcohol according to one of the processes mentioned under the section on preparation of maleic oils; and, the preparation of copolymers with styrene.

Dehydrated castor oil of low viscosity is used in alkyd resin preparations. For oleo-resinous systems an oil with a high viscosity of about 50 stokes is preferred.

High viscosity, in the case of catalytically treated oils is produced by heating the oil further in the presence of the catalyst or after removing the catalyst.

*Table 5. Chemical constants of dehydrated castor oil**

Constants	*Unbodied oils*			*Bodied oils*†	
	Castung 103	*Synthenol*	*Dehydrol*	*Synthenol*	*Castung* 403
Acid no.	4·07	4·38	4·07	4·05	4·44
Colour	3·9	4·5	3·1	5·9	3·7
Vis. (p)	1·8	1·8	7·2	41·7	46·4
Sap. no.	189·2	190·0	190·4	189·0	191·6
Iodine value	132·8	117·4	116·5	133·2	115·6
Spec. gravity	0·9374	0·9384	0·9466	0·9530	0·9547
Ref. index	1·48144	1·48133	1·48422	1·48612	1·48649
Hydroxyl value	25·6	25·3	14·8	12·1	9·25
% diene conjug.	30·58	18·47	18·83	28·59	18·80
Gel. time (min)	58	67	41	24	19
Drying time (h)‡	1 : 30	2 : 0	1 : 48	0 : 54	0 : 54

* Oils available in 1949.
† Bodied at 307°C.
‡ With 0·4% Pb and 0·05% Co naphthenate driers.

The latter method is usually preferred. With oils prepared by processes of esterification and pyrolysis, a polyhydric alcohol can be added to the oil after the pyrolysis reaction is complete, followed by continued heating until the desired viscosity is obtained. As the bodying of the oil proceeds to a viscosity of about 50 stokes, the hydroxyl value becomes neglibible.

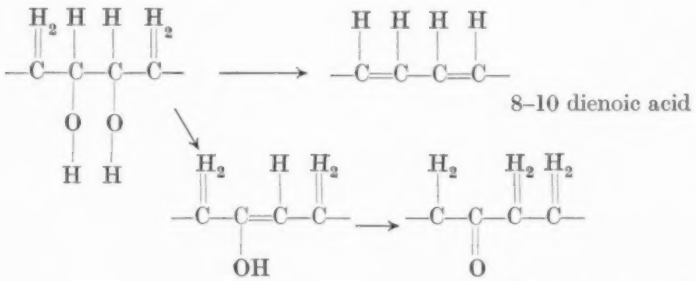
In Table 5 are given typical analyses of a series of dehydrated castor oils available in the United States. In low viscosity oil, the per cent conjugation is not over 31 per cent determined by the ultra-violet spectroscopic method.

Von Mikusch (1949) has described a process which can be used to detect dehydrated castor oil. His method consists of treating oils with an excess of alkali to induce conjugation. In the case of castor oil about 20 per cent of the acids will be isomerized to a 10–12 dienoic acid which can be isolated as a solid and identified as such.

2. *Oxidation and dehydration of dihydroxy acids*

Related to the dehydration of castor oil, is a process applied to dihydroxy fatty acid derivatives. The simplest case involves the preparation of dihydroxystearic acid from oleic acid. The latter can be treated with alkaline permanganate or epoxidized and hydrolysed. The cost involved in these processes is sufficient to discourage any large-scale use. However, epoxidation is now a commercial process for plasticizer oils (Swern, 1954; Terry and Wheeler, 1949, 1951).

Kaufmann and Ganeff (1943) obtained a keto-stearic acid together with the desired 8–10 dienoic acid when dihydroxystearic acid was dehydrated. Previous work (Rheineck, unpublished) showed that the keto-stearic acid could readily be separated by extracting the mixed acids with petroleum ether. This reaction is as follows:



When the 8–10 dienoic acid was esterified with glycerol, an oil was obtained which had drying and film characteristics definitely superior to dehydrated castor oil.

The use of epoxy oils as precursor for conjugated products attracted the attention of Carleton (1950) and Crowder and Elm (1945). Carleton

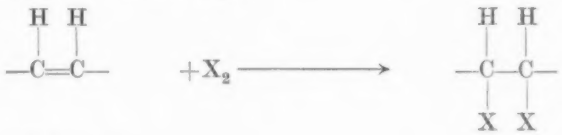
hydrogenated the oils and then flash dehydroxylated them for 1 min at 260–305°C at about 5 mm absolute pressure. The work of CROWDER and ELM took three courses: (a) the epoxy product was treated with anhydrides to yield diacyloxy derivatives which were then pyrolyzed to the diene acid; (b) the oxirane ring was opened by heating the epoxide with an acid and pyrolyzing the resulting hydroxy–acyloxy derivative in the presence of an acid catalyst; and (c) the epoxides were pyrolyzed directly by heating to about 300°C in the presence of catalytic amounts of suitable acids. The oils treated in this manner dry relatively fast, but give films which remain tacky for a considerable time.

COLBETH (1945) showed that a satisfactory drying oil could be prepared by air-blowing an oil at 95°C, to two-thirds of its original iodine value. The hydroxyl groups which were introduced were removed with sodium bisulphate.

3. *Halogenation and dehydrohalogenation*

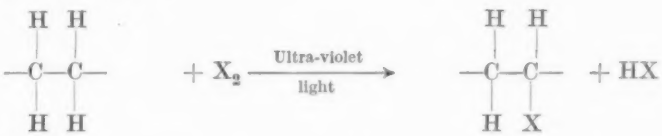
The reactions involved in this section involve preparation of halogenated oils or fatty acids by addition or substitution reactions. There are three general reactions:

Halogenation addition to a double bond



Halogenation at allylic carbon

Halogenation by substitution



TEETER (1952) used the second reaction with success. He treated vegetable oils with tertiary butyl hypochlorite and then dehydrohalogenated the chlorinated oil. Analysis of a pilot-plant run (BELL and TEETER, 1950) on soybean oil before it was thermally dehydrohalogenated showed 20 per cent conjugated unsaturation and about 9 per cent of chlorine. At the end of the run approximately 67 per cent of the chlorine was removed and conjugated unsaturation was increased to about 30 per cent. Mild bases also can be used in the dehydrohalogenation reaction (TEETER, 1952). These processes have not met with any commercial acceptance.

In the early days of World War II it was reported that a 'synthetic' China wood oil, known as 'Trienol' was prepared in Switzerland by the 'Münzel process'. Reports (BLOOM, 1939) said it was made by treating dehydrated castor oil, 'Dienol' with hypochlorous acid. This was then reported to be successively dehydrohalogenated and dehydrated to yield a good drying oil. According to BOLLEY (1949) the Trienol received in the United States was found to be equivalent, if not identical with China wood oil. Other attempts to prepare it were unsuccessful.

4. *Dehydrogenation*

At present there does not appear to be any published method for the dehydrogenation of fats and oils. A review of some of the processes tried has been published by GORDON (1949a).

5. *Catalytic isomerization*

Isomerization of the unsaturation in non-conjugated oils, such as linseed, soybean, and dehydrated castor oils, to the conjugated forms, seemed a logical approach to the China wood oil problem. With the appearance of the work by KASS, BURR and associates (KASS and BURR, 1939; KASS *et al.*, 1939; KASS and NICHOLS, 1950) research on isomerization reactions of oils was stimulated.

Before considering the various methods for isomerization and what is to be expected using non-Oriental oils the composition of the base oils in Tables 5 and 6 should be considered. An inspection of these compositions shows at once that it is impossible to attain the same amount of conjugated triene structure present in China wood oil, without dehydrogenation. At best, these oils when treated to fully conjugate their unsaturation can only approach China wood oil in composition.

Table 6. *Composition of oils compared with china wood oil*

Oil	% *various acids*				*Total conj. (theor.)*
	Sat.	*Mono-olefinic*	*Di-olefinic*	*Tri-olefinic*	
Soybean	13	28	54	5	59
Linseed	10	22	17	51	68
Dehydrated Castor	3	7	87	3	90
China Wood	5	8	4	83*	87

* Actual conjugation.

A number of papers have appeared in the literature covering the chemistry involved in the change from non-conjugated to conjugated oils. Some cover the subject broadly beginning with simple olefins (ARMITAGE and COTTRELL, 1948; BATTLINE, 1943). Other reviewers cover the subject as applied to oils, paints, and their evaluations (BALBI, 1953a; BURR, 1944; COSGROVE and

EARHEART, 1949; COWAN and AULT, 1945; CROSSLEY and HILDITCH, 1952; VON MIKUSH, 1953; VON MIKUSH and MEBES, 1953a,b; NICHOLS *et al.*, 1950; REINHOLD, 1942; SCHAFER, 1953; TALEN, 1950; TOUCHIN, 1946; WALTON, 1950; DE WILDE, 1950) and the kinetics of the isomerization process (COWAN, 1949; NICHOLS, 1950)

Alkali process. Early work on isomerization of oils stemmed from observations of MOORE in 1937. He noticed that normal oils subjected to prolonged saponification showed absorption in the ultra-violet region corresponding to diene conjugation. These observations stimulated study in two directions, namely, further investigation of the use of alkali to effect the change; and, secondly, measurement of the change by ultra-violet absorption spectrograms.

Moore's limited saponification studies were continued by BURR (1941) and his co-workers (KASS and BURR, 1939; KASS *et al.*, 1939). They improved the alkali process to effect a greater degree of conjugation of various fatty acids by use of higher boiling alcohols such as butyl alcohol and ethylene glycol during the saponification. Later, CAWLEY (1944) showed that alcohol ethers were also satisfactory, provided an alcohol hydroxyl group was present with the alkali during the process. Glycerol was also used (RHEINECK, unpublished) to obtain a still higher temperature during the isomerization process. The glycerol process has been described more recently by SLANSKY (1954). A detailed study using ethylene glycol is reported by SPITZER *et al.* (1941).

Because it was recognized that the use of alcohols as solvents was not readily adaptable to plant procedures, aqueous systems under pressure were investigated. Prior to this time it had been felt that the presence of water during the isomerization process with alkali was undesirable and would not give the desired effect. Bradley and co-workers (BRADLEY, 1945a; BRADLEY and RICHARDSON, 1942; STEVENS, 1944) and RHEINECK (unpublished) showed that it was entirely feasible to use aqueous systems at high temperatures. Both alcoholic and aqueous alkali isomerization processes form soaps from which it is necessary to free the conjugated acids with strong mineral acids. In the alcoholic process it is essential to remove the alcohol before acid treatment to prevent re-esterification. In the case of the aqueous high-pressure process this complication is absent.

From the alkali isomerization processes, certain facts were deduced which in aggregate virtually precluded any extensive commercial development of alkali-isomerized oils:

(a) High temperatures (160°C or higher) are necessary. (The pressure developed in the aqueous process is incidental.)
(b) The reaction time at any temperature to obtain maximum conjugation is critical because the percent conjugation seems to pass through a maximum under prolonged processing.
(c) Results with soybean oil are generally more reproducible than those with linseed oil.
(d) As measured by ultra-violet absorption, the theoretical maximum of conjugated acids is never obtained.

(e) Flash distillation of conjugated acids is preferred to the batch method. This holds polymerization of the more reactive components to a minimum.

(f) Esterification of the conjugated acids by glycerol and processing to varnishes does not give as much improvement in the products as was anticipated. (ARCHER-DANIELS-MIDLAND, unpublished; RHEINECK, unpublished)

(g) The cost of the oil produced is too great to encourage large scale production Furthermore, the advantages gained are not commensurate with the costs involved.

(h) Performances in varnishes equivalent to that of the isomerized oils can be attained by other oil and resin modifications at lower costs.

Isomerized linseed and soybean oils prepared by the Woburn Chemical Company appeared on the market in the early 1940s under the trade names 'conjulin' and 'conjusoy'. It has been reported recently by VON MIKUSCH (1950) that these oils were prepared by an alkali isomerization process operated on a continuous basis. They are probably similar to the oils prepared by BRADLEY and RICHARDSON (1942) using the aqueous high pressure method.

Some typical constants of conjugated acids prepared by BRADLEY and RICHARDSON (1942) are shown in Table 7. In another study (ARCHER-DANIELS-

*Table 7. Initial alkali isomerization experiments**

Fatty acids (g)		*alkali* (g)		*Water* (g)	*Time*† (h)	% *conjugation*	
						Diene	*Triene*
Linseed	75	KOH	75	100	2·0	34·6	7·66
Linseed	75	NaOH	75	125	3·0	41·0	8·20
Soybean	100	KOH	75	110	2·5	20·2	1·33
Sardine	75	LiOH	100	100	3·5	23·2	8·00
Dehydrated Castor	75	LiOH	75	100	3·0	41·7	0·75

* According to BRADLEY and RICHARDSON (1942).
† At 225°C.

MIDLAND, unpublished) linseed oil treated with twice the theoretical quantity of 25 per cent aqueous sodium hydroxide for 2 h at 200°C yielded acids with the following constants:

Conjugated diene acids	= 23·2 per cent
Conjugated triene acids	= 36·6 per cent
Total	59·8 per cent
Conjugated acids, theoretical maximum	= 68 per cent
Acid value	= 195
Iodine value	= 142

There are other variations of the alkali isomerization process. LUACES (1945) used sodium methoxide as the catalyst. KIRSCHENBAUER (1945b) disclosed a

method whereby an oil is heated with alkali in the absence of water. Another method is described by RHEINECK and CRECELIUS (1944b) in which soaps are dispersed and heated in rosin to induce the double bond shift. When the reaction is completed the soaps are decomposed with mineral acids or monochlorohydrines. The latter react further with the rosin and fatty acids to yield varnishes.

Although none of these procedures has been used to any great extent commercially, study of the isomerization reactions led to a very worth-while application in analytical procedures for determining the fatty acid composition of oils. The original method of MOORE (1937) was studied and further developed by BURR and his co-workers (BURR, 1941; HOLMAN and BURR, 1948; NORRIS *et al.*, 1941; NORRIS *et al.*, 1943; SCHNEIDER *et al.*, 1949) BRADLEY and RICHARDSON (1942) and by BRODE *et al.*, (1944). It was developed specifically as a quantitative analytical tool by MITCHELL *et al.* (1943), and O'CONNOR *et al.* (1945). Improved heating equipment for analytical work is described by LIPS and TESSIER (1949) and by VANDENHEUVEL and RICHARDSON (1953).

The original spectroscopic method was directed to determining dienoic and trienoic acids. However, in fish oil, tetraenoic acids are present, as LAMBERT and ANDREWS (1948) demonstrated. SWAIN and BRICE (1949) and GROOT and MONNIKENDAM (1949) feel that with some oils the latter probably originates from autoxidation products produced in the oils. To compensate for this PRIVETT and LUNDBERG (1951) determined a correction factor.

For analytical procedures, HOLMAN and BURR (1948) report that the maximum isomerization can be produced by treating acids with ethylene glycol containing 22–23 g of KOH/100 ml for 8 min at 178°C. Similarly, HERB and REIMENSCHNEIDER (1952) and HAMMOND and LUNDBERG (1953) heated samples in 21 per cent KOH in ethylene glycol for 15 min at 180°C for determination of arachidonic and docosahexaenoic acids. For more detailed treatment of spectrophotometric analysis of fats, see Vol. 4 of this series.

*Table 8. Conjugation produced on drying oils with 1–2% nickel on carbon catalyst**

Oil	*Time* (h)	*Temp* (°C)	% *conjugation*
Soybean	6	160	20·1
	6	170	32·1
	4	180	34·9
	4	190	37·7
Linseed	6	160	24·7
	6	170	28·0
	4	180	32·5
	4	190	33·3
Dehydrated castor	4	175–185	38·3

* According to RADLOVE, TEETER and COWAN (1945).

Catalytic methods. Those familar with the alkali isomerization process soon recognised its definite limitations, and work was focused on processes which would not split the oil, and preferably also not body it. These efforts are described by RADLOVE, TEETER and COWAN (1945). They disclose the preparation of nickel catalysts, their use, recovery and effect on oils. Typical results are shown in Table 8.

Evaluation of such nickel-conjugated oils in paints and varnishes is also described (FALKENBERG *et al.*, 1946; LEWIS *et al.*, 1950). In a later paper

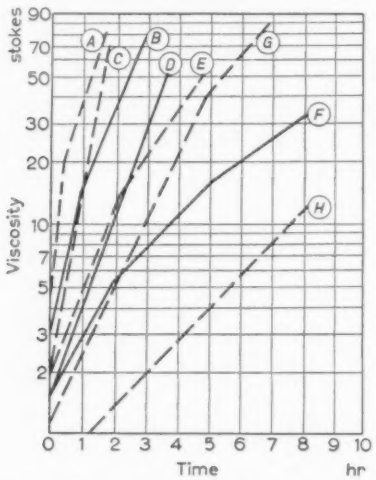


Fig. 3. Bodying of isomerized linseed and soybean oil as compared to dehydrated castor oil. A. isomerized† linseed oil bodied at 310°C; B. isomerized linseed oil bodied at 293°C; C. Dehydrated castor oil‡ bodied at 310°C; D. dehydrated castor oil bodied at 293°C; E. isomerized soybean oil§ bodied at 310°C; F. isomerized soybean oil bodied at 293°C; G. refined linseed oil bodied at 310°C; H. refined soybean oil bodied at 293°C.
* According to FALKENBURG *et al.* (1946).
† Contains 22·4% diene and 6·6% triene conjugation.
‡ Contains 22·1% diene conjugation.
§ Contains 27·7% diene and 2·8% triene conjugation.

(RADLOVE *et al.*, 1946) these investigators point out that other catalysts such as platinum and palladium on carbon are also effective.

The following variations in the use of nickel catalysts were investigated: nickel on kieselguhr (MASUNO *et al.*, 1950) nickel plus palladium (GORDON, 1949b) nickel poisoned with sulphur (SANA, 1953) nickel silicate and sulphur (STEJSKAL, 1950) nickel–cobalt (LEVER BROS. and UNILEVER LTD., 1953) cobalt (BLASER and STEIN, 1952). As in the alkali process, the degree of conjugation produced by the nickel catalytic process was insufficient to improve oils to the desired extent.

The work of FALKENBURG *et al.* (1946) showed that catalytically conjugated oils have increased heat-bodying rates compared to non-isomerized oils, as shown in Fig. 3.

Iodine and various iodine containing compounds have been used in isomerization reactions. MCNICOLL (1949) treated oils with elementary iodine until a

constant refractive index was attained and then used zinc dust to remove the iodine. Conjugation in oils so treated was reported as follows: linseed 40–43 per cent, soybean 34–38 per cent, corn oil 33 per cent, and sesame 30 per cent. A similar process is disclosed by RALSTON *et al.* (1950).

A variety of iodine compounds have been described by RALSTON and TURINSKY (1946) for isomerization of oils: (a) amine hydroiodides, aromatic amine hydroiodides and ammonium iodides, (b) aliphatic iodides, e.g. dodecyl iodides and terpene iodides, etc. and (c) non-metallic iodides, e.g. phosphorous triiodide, and antimony triiodide. COWAN (1949) is of the opinion that iodine compounds are the most promising of the catalysts for conjugation. He claims to have duplicated Ralston's results (Table 9).

Table 9. Conjugation of soybean oil by various iodine compounds disclosed by RALSTON *and* TURINSKY*

Catalyst	*% conjugation*		
	Diene	*Triene*	*Total*
CH_3I	16·2	2	18·3
AlI_3	28	4·97	33·33
PI_3	26·9	4·63	31·79
Turpentine + iodine	31	0·12	31·12

* According to data obtained by COWAN (1950).

WATERMAN, VAN VLODROP, and co-workers (VAN VLODROP, 1941; WATERMAN and VAN VLODROP, 1940; WATERMAN *et al.*, 1940, 1948) treated linseed oil with gaseous and liquid sulphur dioxide in research initiated prior to the war. They described the ultimate product as resembling China wood oil in maleic anhydride values, drying characteristics, and reactivity with phenol (WATERMAN *et al.*, 1940). BOELHOUWER (1953) stated that oxygen is necessary in the process to activate the system prior to conjugation. In later work (WATERMAN and VAN VLODROP, 1942) on sulphur dioxide treated oils, the products were fractionated and polymerized.

Detailed information on the use of sulphur dioxide is given by CANNEGIETER (1947). Polymerization constants were determined for different oils and concentrations of sulphur dioxide. Since the rate of polymerization of unconjugated oils was appreciably increased, as compared with conjugated oils, CANNEGIETER concluded that this treatment induced isomerization. Fig. 4 shows the effect of sulphur dioxide flow on the bodying rate of linseed oil at 300°C.

Recently BOELHAUWER *et al.* (1950) demonstrated that treatment of linseed oil with atomic hydrogen increased viscosity, led to some hydrogenation and gave measurable conjugation. Use of a silent discharge for producing conjugation is described by YZU and VIAN (1950).

The effects of heating oils with the following oxides and earths to produce conjugation has been studied: (a) aluminium oxide (TURK and BOONE, 1944; COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, 1954) (b) magnesium oxide (ZETTLEMOYER and WALKER, 1954) (c) Fuller's earth (SLANSKY, 1947; TSUCHIYA and OHKUBO, 1952), and (d) silicates (SLANSKY, 1947; TURK and BOONE, 1946). Comparative data in Table 10 show the effect of earths and carbon in

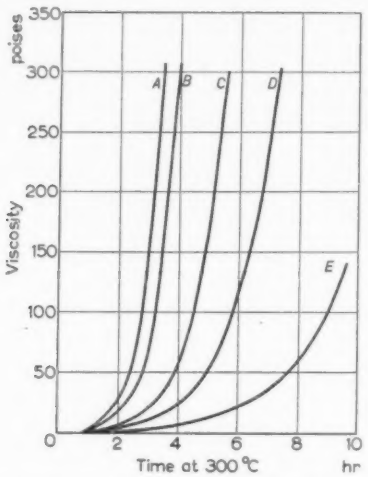


Fig. 4. Typical bodying rate curves for linseed oil at 300°C treated with sulphur dioxide according to CANNEGEITER (1953)
A—215 g SO_2/100 l./h; B—100 g SO_2/100 l./h; C—80g SO_2/100 l./h; D—25 g SO_2/100 l./h; E—Control

producing conjugation. It is COWAN's (1949) opinion that particle size of these compounds governs their isomerizing effect. IVANOVA and PETROVA (1949) state that finely divided zinc, mercury, iron, calcium and lead will produce conjugation. Phosphotungstic acid is also used (VARLAMOV and SLOZINA, 1953).

Table 10. *Conjugation produced in soybean methyl esters with surface active agents at* 210–220°C*

	% catalyst	*% diene conjugation*
None		1
Acid-washed kieselguhr	23	11·3
Nuchar XXX	23	12·8
Florex XXF	10	3·9
Activated alumina	23	4·7
Ni on kieselguhr	30	17·3

* According to COWAN (1949).

RADLOVE (FALKENBURG *et al.*, 1948; RADLOVE, 1951) showed that it was possible to produce conjugation in soybean oil by heating with anthraquinone. The data indicate that 18–24 per cent conjugation is possible in either linseed or soybean oil by this treatment.

NOVAK (1943) claimed to have produced conjugation by air blowing. COLBETH (1945) described a method whereby an oil is blown to two-thirds of its iodine value at about 95°C, and then heated under a vacuum to about 260°C when a gas is evolved. This product is then dehydrated with sodium bisulphate to give a conjugated oil.

FARMER, KOCH and SUTTON (1943) discovered in their studies that non-conjugated systems are converted to the conjugated under the influence of oxygen during the air-drying processes. GUNSTONE and HILDITCH (1945) showed a relationship between conjugation and peroxide values. No practical use was made of this observation until WEIBE (1952) disclosed his results on the peroxide treatment of oils. The beneficial effect appears to be specific for di-*tert*-butyl peroxide. Benzoyl peroxide does not produce a beneficial effect. The influence on the drying characteristics of sardine oil are shown in Table 11. CLINGMAN and SUTTON (1953) showed that it is possible to produce conjugation and dehydro-polymers by reacting methyl linoleate with di-*tert*-butyl peroxide.

Table 11. *Effect of di-tertiary-butyl peroxide treatment on the drying of sardine oil**

Oil constants	*Treated†*	*Untreated*
Viscosity (G—H)	O–P	A
Iodine val.	153	183
Mol weight	925	897
Refractive index N_D^{20}	1·4856	1·4818
Drying time‡		
Set	1 h	4 h
Dust-free	1·5	5·5
Tack-free	2	6·5
Hard	4	50 +

* According to WIEBE (1952).
† Treated with 5% peroxide.
‡ With 0·05% cobalt octoate.

III. SYNTHETIC OR RECONSTITUTED OILS

A. Introduction or substitution of polyols

Based upon the functionality concept, improvement of drying oils is possible if glycerol is replaced by polyols having a greater number of esterifiable hydroxyls. This section reviews work which has been undertaken to evaluate polyols as oil upgraders to enhance drying properties.

Synthetic oils have been prepared by the generally employed esterification methods of organic chemistry: (a) direct esterification of fatty acids and an alcohol; (b) interchange methods (alcoholysis, acidolysis, inter-esterification); (c) use of acid chlorides in the presence of a tertiary amine and alcohol; and (d) use of fatty acid anhydrides and alcohol.

Each of these methods has definite limitations. Method (a) at present is of great practical importance. With increased knowledge of the reactions and physical properties of fats and oils, method (b) promises to have increasing practical value. Methods (c) and (d) are indirect in that preliminary derivatives must be prepared, which add to the cost of the processes. Method (c) is useful in processes in which one of the reactants, e.g. carbohydrates, is unstable to heat, or in which the final product, e.g. a China wood oil fatty acid ester of a higher alcohol, has strong gelation tendencies.

In method (a), the process is carried out either in closed systems under vacuum or in open equipment. In the fusion method, water is removed by vacuum or by an inert gas such as carbon dioxide or gas-engine exhaust. In the solvent process water is removed by azeotropic distillation. Temperatures used are in in the range of 180–220°C. When a dual effect of esterification and polymerization is wanted, higher temperatures are used.

Inert gas passing though the mixture serves as a means of agitation and water removal. It is pointed out by JORDAN (1943) that the use of steam, rather than carbon dioxide, in the reaction favors etherification rather than esterification, as measured by the relationship between acid value and hydroxyl content. It is common experience that the use of carbon dioxide with this reaction displaces the equilibrium of esterification reaction so that oils with much lower acid value result, than when steam is used in an analogous composition.

The azeotropic method described by RABIN and EARHART (1943) is widely used for esterification reactions. The presence of solvent such as xylene, mineral spirits, or the equivalent, with different boiling points, has beneficial effects. Losses and colour degradation because of local overheating are reduced. Colour can also be improved by using anthraquinone (CORN PRODUCTS REFINING Co., 1953).

In some instances it has been found that catalysts are beneficial in accelerating esterification. KONEN *et al.* (1945) made a comparative study of the use of catalysts in the esterification of linseed acids with various polyhydric alcohols and found that in general, the initial esterification rate was increased, but the total time required to attain acid values below 5 was the same, with or without catalysts. Moreover, acid catalysts darkened the colour, camphor-sulphonic acid being the least objectionable of those tried, whereas alkaline earth metals and their compounds had the least effect on colour. They noted that sulphur dioxide seemed beneficial in the early stages of the reaction and could be used to agitate the mass.

When catalysts are used, it appears to be generally true that there is a loss in colour. Calcium acetate in alcoholysis reactions is the least objectionable in this respect. According to JORDAN and WITTCOFF (1951) dibasic acids, e.g.

phthalic and adipic, may be added to the reaction mixture on cooling to remove the basic catalysts and improve colour after filtration. SPILLER and BAMBERGER (1954) suggest the use of triphenyl phosphite and phosphoric acid to remove catalysts and improve colour. This is especially useful in alkyd resin work.

It has been suggested (RHEINECK, unpublished) that addition of 5–10 per cent of acetic anhydride at an acid value of approximately 10 will lead to rapid completion of esterification. At this point, the excess anhydride and free acetic acid are removed by distillation. A ketene sparge also serves the same purpose.

REID (1951) has reviewed methods of esterification for many types of compounds not involved in the preparation of coating vehicles and products. Methods for evaluating polyols for protective coating products have also been reviewed (STAFF REPORT, 1953a). The remainder of this section will deal with the large number of polyols used to prepare synthetic oils. (Vinyl and polyvinyl esters are discussed in a separate section.) The methods described are adaptable to production processes.

B. Evaluation of individual polyols

Ethylene glycol (CH_2OHCH_2OH). This alcohol esterifies quite readily between 180–220°C, but care must be exercised to prevent its loss by distillation with the water of esterification.

The non-conjugated fatty acid esters of this alcohol do not dry; on the other hand, drying occurs in esters of acids with conjugated bonds, e.g. China wood oil acids. In protective coatings glycol esters are of no particular value. Glycol is sometimes used in conjunction with pentaerythritol to approximate the properties of glycerol esters.

Glycerol ($HOCH_2CHOHCH_2OH$). Natural fats and oils are almost without exception esters of this alcohol. There are innumerable papers on its esterification. The polyol itself finds its widest application in alkyd resins. It can be readily esterified with fatty acids between 180–220°C in an inert atmosphere. In the early stages of the reaction, there is a tendency for the glycerol to distill and precautions must be taken to prevent this. The secondary hydroxyl group is more difficult to esterify than the two primary hydroxyl groups.

Glycerides prepared by esterification of fatty acids show improved drying characteristics over the natural oils from which the fatty acids are derived. Synthetic glycerides dry without the usual induction period found in natural oils and attain greater film hardness. There may be two reasons for this: (a) the naturally occurring antioxidants in the oil are removed during the preparation of the fatty acids; or, (b) more complex polyglycerols are formed in the esterification mixture.

Properties of glycerides derived from fish oil acids have been described by STINGLEY (1940). These are primarily the esters of the unsaturated fish oil 20 and 22 carbon fatty acids with iodine values as high as 250 at the beginning of the esterification process. Aside from these fish-oil derived synthetic glycerides, and the Scheiber oils, no synthetic triglycerides have found commercial acceptance as drying oils.

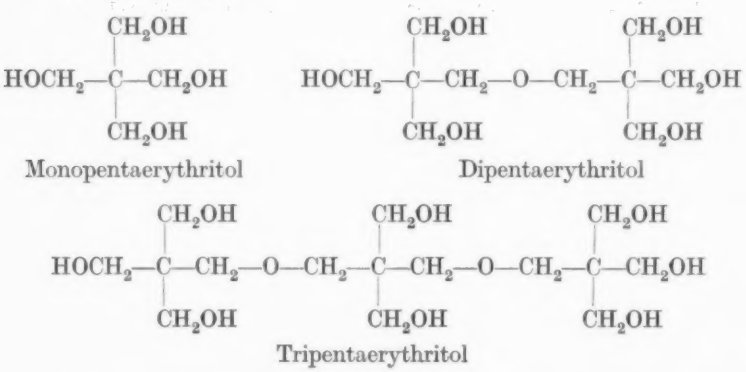
Glycerol finds a very wide use in alcoholysis reactions for the preparation of monoglycerides and diglycerides which are converted into alkyd resins and varnishes by further reaction with dibasic acids, resin acids, and other materials.

Polyglycerol esters may be formed unintentionally during the esterification of glycerol but STRAUSS (1940) describes the preparation of these esters by direct reaction of fatty acids and polyglycerols. The NORTHWESTERN PAINT AND VARNISH PRODUCTION CLUB (1950) evaluated polyglycerol esters and showed them to be better than corresponding glycerol esters and about equal to pentaerythritol esters.

Erythritol ($HOCH_2CHOHCHOHCH_2OH$). This tetrahydroxy alcohol has been used in oil work only in basic studies. It was synthesized by HIMEL and EDMUNDS (1951) by treating butadiene with hydrogen peroxide in methyl formate. It has never been available in commercial quantities at a sufficiently low price to warrant extensive investigation.

Precautions to prevent loss as in the preparation of glycerol esters are not necessary. The alcohol is more difficult to esterify than glycerol because it contains two secondary hydroxyl groups. RHEINECK and BRICE (1954) prepared the linseed fatty acid esters of erythritol and found that they showed somewhat better drying characteristics than a similar pentaerythritol ester. This may have been caused either by the presence of secondary alcohol esters or by a slight amount of bodying due to longer esterification time.

Mono-, di-, poly-pentaerythritols.



These alcohols are by far the most important in drying oil syntheses, varnish work, and alkyd resins. The alcohols of this family have been used to a greater extent than any other polyhydric alcohols, especially in the preparation of varnishes by the '*in situ*' or 'uniphase' method. There are several reasons for this: (a) they have economic advantages; (b) the esters are advantageous in drying characteristics and bodying rates; (c) the esterification is rapid and easy, because all of the hydroxyl groups are primary; and (d) loss of polyol during esterification is less than for other available polyols.

Reaction of formaldehyde with acetaldehyde produces a mixture of monopentaerythritol and higher polymers. This product is sold as 'technical'

pentaerythritol. Separation techniques give a 'pure' grade which analyses at least 99 per cent monopentaerythritol with dipentaerythritol and higher polymers as impurities. The polymers were formerly marketed as 'polypentaerythritol' but they now may be separated further, to give dipentaerythritol. Although the di- and polymeric products produce protective coating products with definitely superior properties, the small volumes available have discouraged the interest of large oil producers. No attempt has been made to modify the pentaerythritol synthesis to produce only the di- and poly-pentaerythritols on a large scale.

Esters have been prepared by both direct esterification (BURRELL, 1945; BURRELL and BOWMAN, 1945; KONEN *et al.*, 1945) and alcoholysis methods (BURRELL, 1944). The comparative esterification rates of pentaerythritol and other polyols are shown in Fig. 5. As may be seen, the pentaerythritols are more rapidly esterified than other available polyols.

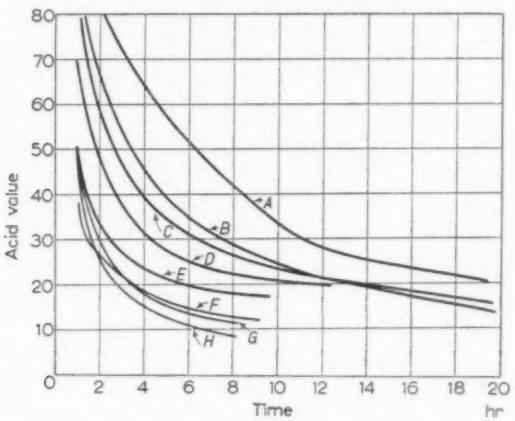
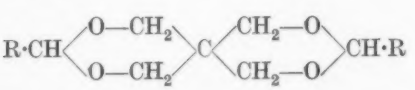


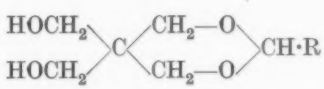
Fig. 5. Esterification curves for soya fatty acids and polyhydric alcohols with equivalent amounts of fatty acids at 235°C according to RHEINECK and BRICE (1954).
A—inositol; B—quebrachitol; C—pinitol; D—erythritol; E—glycerol; F—monopentaerythritol; G—tripentaerythritol; H—dipentaerythritol.

The drying of pentaerythritol esters can be improved by separating the lower-molecular-weight products by an alcohol extraction method, according to BRADLEY (1944a).

Pentaerythritol oils of linseed and soybean fatty acids have appeared on the market. Pentearythritol soybean esters seem to be useful in house paints. A linoleum binder based on polypentaerythritol is described by FISCELLA (1953).

Related to the pentaerythritols are their acetals, e.g. the formal, acetal and butyral.

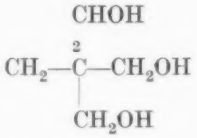




where R = CH_3, C_2H_5 and C_4H_9

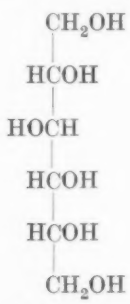
Partial esters of these, i.e. the acetates, resinates and linolates, are described by BARTH (1948), for use as plasticizers.

Trimethylolethane. This polyol is related to the pentaerythritols and is made by an analogous process.

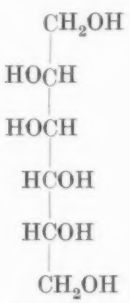


It has recently become available in sufficient quantities to encourage large volume uses. With drying oil fatty acids the esterification rate of trimethylolethane is intermediate between glycerol and pentaerythritol (HEYDEN CHEMICAL CORP, 1953). The bodying rates of the esters are also intermediate.

Sorbitol and mannitol. These polyols are made by the reduction of glucose.



Sorbitol



Mannitol

About 1934 commercial lots of sorbitol contained considerable amounts of reducing sugars. These impurities caused difficulties in esterification reactions. The usual result was a product which contained considerable charred matter. Since about 1940, the quality of this material has been improved so markedly that it is used in the preparation of synthetic oils and '*in situ*' varnishes. The method for esterifying sorbitol is described by BRANDNER *et al.* (1945).

Not all the hydroxyl groups in this polyol are available for esterification. Internal loss of water reduces available hydroxyls to 4,1 primary and 3 secondary. When this alcohol is used in '*in situ*' varnish (RHEINECK, unpublished) an average of $3\frac{1}{2}$ hydroxyl groups are considered to be available. For the esterification of fatty acids 4 hydroxyls are normally considered available but TAKAHASHI and TAKESHITA (1953) state that 4·8 hydroxyls can be esterified at 200°C in 10 h.

Sorbitol esterifies at a slower rate than the pentaerythritols as indicated in Fig. 6. This slower rate is undoubtedly attributable to the secondary hydroxyl groups. The esterification product of sorbitol is not a true sorbitol ester. It is an ester of a sorbitan, produced by internal dehydration to give ether linkages. The 'sorbitol esters' appear to have drying qualities approximately the same as the corresponding pentaerythritol esters.

Mannitol esters have also been studied (RHEINECK, unpublished). In the early work this polyol did not produce charred material and reacted readily to form satisfactory esters which appeared to be identical with present quality sorbitol products. Mannitol is not now used to any extent in coating vehicles.

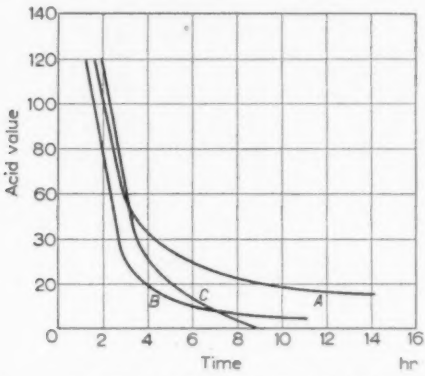
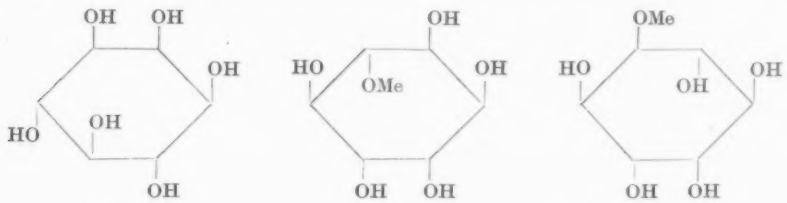


Fig. 6. Esterification curves for linseed fatty acids and polyhydric alcohols at 235°C according to KONEN, CLOCKER and COX (1945)
A—sorbitol (4 : 1 molar ratio); B—pentaerythritol; C—glycerol.

Cyclitols. The naturally occurring cyclic polyols include inositol, pinitol, and quebrachitol which have the following structural formulae:



i-inositol (+)-pinitol (—)-quebrachitol

Inositol is found combined in phytic acid in corn steepwater and soybean and linseed processing by-products. The potential quantities of this polyol are great, but the method of recovery is difficult and costly. Pinitol has been recovered by ANDERSON (1953) from stumps of western Sugar pine, *Pinus lambertiana Dougl.*, in pilot-plant quantities. Quebrachitol (VAN ALPHEN, 1951) is obtained from natural rubber, *Hevea* latex serum. Pinitol and quebrachitol are isomeric monomethyl ethers of inositol.

Inositol. Esters of the solid polyol inositol were prepared in coating vehicles before World War II (RHEINECK, unpublished), but it is not known which isomer was used. Inositol esterifies slowly requiring temperatures as high as 260°C; it appears that an average of about $4\frac{1}{2}$ hydroxyl groups esterify. A portion of inositol remains unreacted possibly because a non-reactive isomer may be formed in the process. The presence of unreacted polyol was observed by RHEINECK and BRICE (1954) and GIBBONS and GORDON (1950).

Linseed fatty acid inositol esters yield air-dried films approximately equivalent to polypentaerythritol esters.

The preparation and properties of pinitol and quebrachitol linseed fatty acid esters are described by RHEINECK and BRICE (1954), who treated the two polyols as equivalent. The esterification curves in Fig. 5 indicate quite conclusively that they are much more difficult to esterify than the control esters, namely, the several pentaerythritols, erythritol and glycerol. These differences in esterification rates are caused by slow reaction of secondary hydroxyl groups.

*Table 12. Sanderson drying times of polyol-linseed fatty acid esters**

Polyol	*Molar ratio fatty acids to polyol*	*Unbodied esters*		*Esters bodied to Z_2 (Gardner)*	
		Set-up time (h)	*Drying time* (h)	*Set-up time* (h)	*Drying time* (h)
Inositol	6	3	5·25	3·3	8·25
	5	2·75	8·0	4·5	8·0
	4	3·75	8·0	8·5	13·0
Pinitol	5	3·33	5·8	3·5	6·25
	4	5·75	8·25	15·0	15·5
	3	11·5	17·0	12·0	14·0
Quebrachitol	5	3·0	7·5	4·0	6·5
	4	3·3	9·0	6·6	9·0
	3	10·0	18·5	5·6	9·0
Monopentaerythritol	4	3·3	6	2·6	2·6
Dipentaerythritol	6	4·25	5·5	1·5	2·0
Tripentaerythritol	8	2·5	3·0	1·5	3·0
Glycerol	3	—	24 +	—	—
Erythritol	4	3·25	4·33	1·75	2·25

All oils treated with 0·5% Pb, 0·05% Co, 0·05% Mn, and 0·01% Ca as driers.
* According to RHEINECK and BRICE (1954)

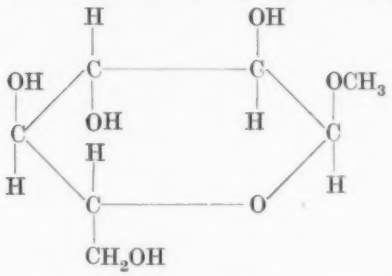
The drying properties of both unbodied and heat-bodied esters are shown in Table 12. There appears to be a direct relationship between the drying properties and the number of hydroxyl groups esterified on any one of the several polyols. The dried film characteristics of the cyclitol esters do not show any advantages over the linseed pentaerythritol esters.

At the present time there is no economic or technical advantage in using these polyols.

Mono- and di-saccharides. In this family of alcohols, glucose, fructose, sucrose and their isomers are considered. Because they caramelize and char at high temperatures they cannot be esterified by the direct methods described for other solid alcohols. High temperatures must be avoided, and indirect methods with acid chlorides and tertiary amines, such as pyridine, have been used (RHEINECK *et al.*, 1938). The ingredients are held at room temperature for about 24 h, after which the oil is recovered and thoroughly washed.

A series of linseed esters prepared from acid chlorides and sugars did not dry as well as esters prepared by direct esterification from conventional polyols. Esters of this type have not had practical value.

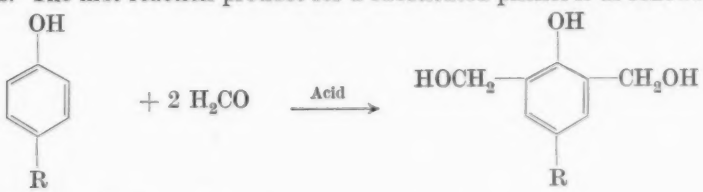
Alpha methyl glucoside. This polyol is made by reacting glucose with methanol.



In connection with the work on the preparation of esters of glucose and fructose in 1940 (RHEINECK, unpublished) it was found that if the aldehyde or ketone group was blocked by methylation the corresponding glucosides could be esterified directly, and further heating of the ester did not result in decomposition. Alpha-methyl-*d*-glucoside has recently become available at such a cost that attempts have been made to encourage its use as a substitute for pentaerythritol (CORN PRODUCTS REFINING CO., 1954).

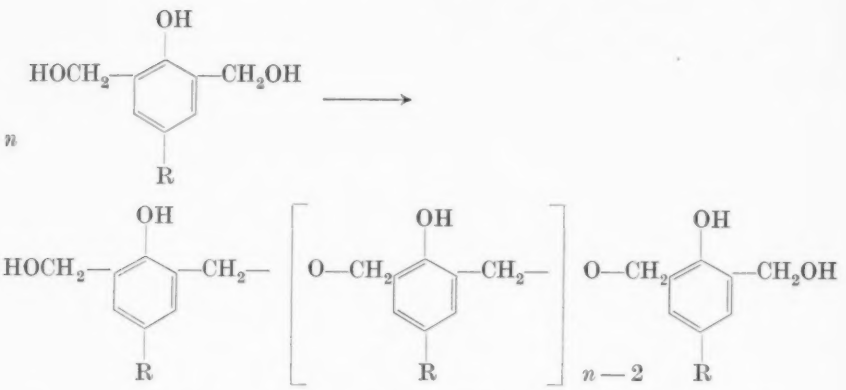
Its esters have been made by several methods. WOLFF and HILL (1948) prepared esters of methyl glucoside by alcoholysis with methyl esters of linseed fatty acids. They concluded that the acetal group is more difficult to hydrolyse than the ester group and they were unable to esterify all the hydroxyls completely. Direct methods for esterifying this polyol are described by GIBBONS and co-workers (CORN PRODUCTS REFINING CO., 1954; GIBBONS and GORDON, 1950; GIBBONS *et al.*, 1953). Their method employs refinements needed to attain minimum colour. Methyl glucoside esters yield dried films of about the same quality as glycerol-pentaerythritol mixed esters.

Phenol–formaldehyde polyols. Methylols which are the reaction products of phenols and formaldehyde with an acid catalyst, have been investigated as polyols. The first reaction product for a substituted phenol is as follows:



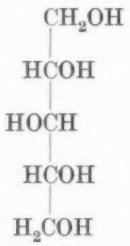
where R is an alkyl group.

The hydroxyls which form a part of the methylol groups have been considered unesterifiable. HARRISON (1952) showed that these methylol derivatives could be reacted with fatty acids in the presence of phosphite esters as esterification catalysts. If the final product of the first reaction is dehydrated, resinification takes place as follows (the preferred range of n is about 4–10)



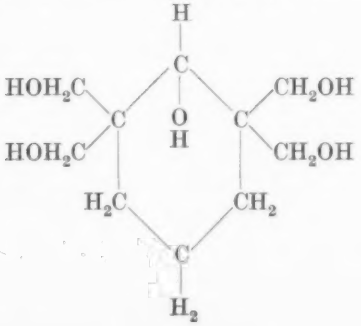
RENFREW (1954) describes an extension of the work of Harrison. In this case the final resinous product of the above equation was also esterified with drying oil fatty acids. An ester prepared from a substituted phenol, polymerized to contain 4–10 phenols units, is described as having drying properties.

Xylitol. TEETER *et al.* (1951) prepared this polyol by the reduction of xylose. The structure is as shown:



When a series of soybean and linseed fatty acid esters was prepared, it appeared that about 4 of the 5 hydroxyl groups of the xylitol were esterified, one group being lost by dehydration. They evaluated these esters in paints and found that they were superior to the corresponding glycerides, especially in the case of soybean esters.

2,2,6,6—Tetramethylol cyclo*hexanol.* This polyol has the following structure:



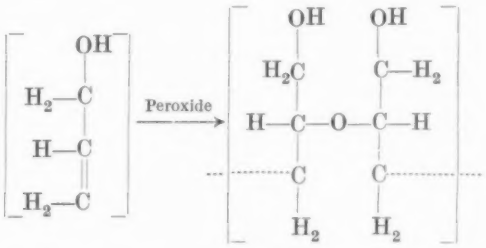
WITTCOFF (1949a,b,c) synthesized it by the reaction of formaldehyde with *cyclo*hexanone, employing lime as a catalyst. This reaction is analogous to that used for synthesis of pentaerythritol.

There are four hydroxyl groups available in this alcohol for esterification. The hydroxyl resulting from the reduction of the ketone group is too hindered to be esterified. A series of esters of this polyol was prepared and compared with pentaerythritol drying oil esters. The tetramethylol *cyclo*hexanol esters dry slightly faster but the ultimate film properties of both are practically the same.

Polyallyl alcohols. Esters of polyallyl or allyl alcohol can be made either by polymerization of the allyl esters of the fatty acids, or by polymerization of allyl alcohol followed by esterification with the fatty acids. The first procedure is not very satisfactory, especially for unsaturated esters, as described by HARRISON and WHEELER (1951).

In the immediate post-war period the Shell Development Co. prepared a series of polyallyl alcohols which contained, on the average, between 6 and 10 hydroxyl groups per molecule. Polyallyl alcohols can be prepared by peroxide polymerization according to ADELSON and GRAY (1945).

These alcohols contained some oxygen linking according to the following reaction :

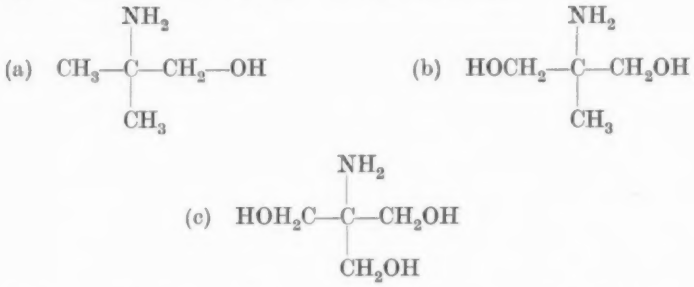


BRADLEY (1945) prepared esters of polyallyl alcohol and indicated that as limiting conditions there should be at least 5 hydroxyls on the polyol and an iodine number of at least 100 for the acids in order to obtain good drying properties. These esters can also be improved by alcohol extraction. Alkyd type esters are disclosed by PFANN and KROPA (1952). Polyallyl alcohol esters prepared by direct reaction and by alcoholysis were evaluated by COX *et al.* (1953). The properties of soybean esters of polyols with between 8 and 16½ hydroxyls on the average are shown in Table 13. It is apparent that both oil drying and gelation characteristics improve with polyallyl alcohol hydroxyl content. Improvements in film properties are also related directly to alcohol functionality.

Allyl and substituted allyl esters of dimerized soybean acids were polymerized with aluminium chloride catalyst by TEETER and COWAN (1945). These reaction products are suggested as softening agents.

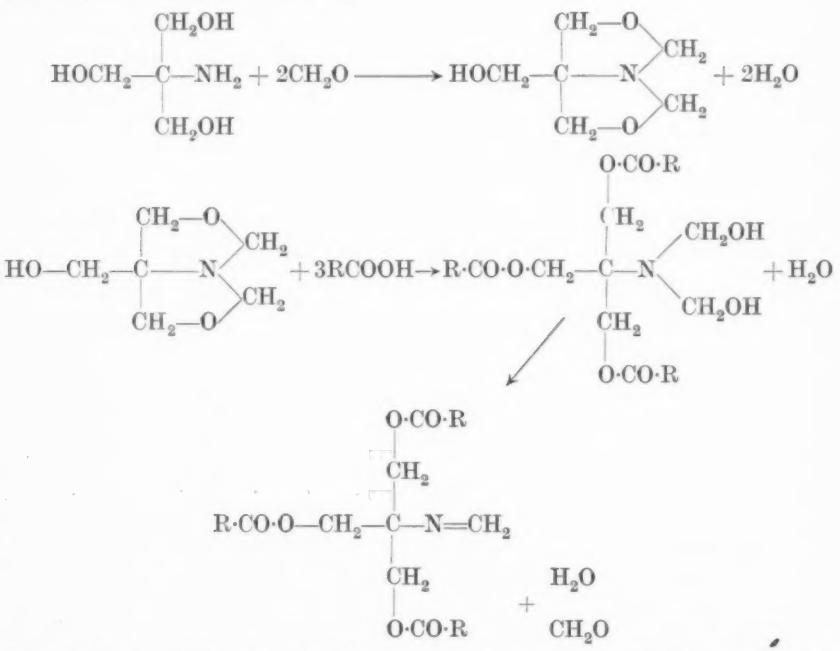
Amino alcohols. In this section, the discussion is limited to the reaction products of the fatty acids with the following amino alcohols: (a) 2-amino-2-methyl-1-propanol; (b) 2-amino-2-methyl propandiol; (c) tris-(hydroxy-methylol) amino-methane.

These alcohols, are made by reaction of nitromethane, nitroethane and nitropropane with formaldehyde followed by reduction:



The final esterification products of these polyols are thought to be ester-amides. LYCAN and EYRE (1945) describes the general methods which can be used to prepare drying oil products. It is also stated that they dry tacky, but have high moisture resistance. Treatment of the amino alcohol with formaldehyde before esterification (AMERICAN CYANAMID Co., 1944) or formaldehyde treatment of the finished ester (JORDAN and SHAPIRO, 1951) will prevent tackiness and produce a hard product on drying.

The formaldehyde reaction, and esterification, is stated to be as follows (AMERICAN CYANAMID Co., 1944):



In or about 1944, oils of this type were proposed as China wood oil replacements. They produced very durable films when cooked into varnishes

Table 13. *Polyallyl alcohol esters of linseed and soybean fatty acids**

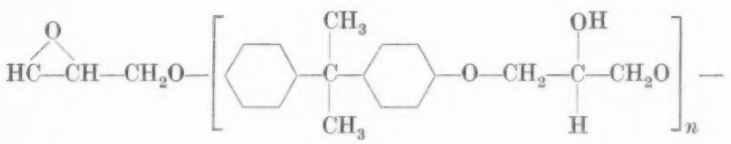
Reactants	*Product number*				
	1	2	3	4	5
Linseed acids	75·3	76·5	78·3		
Soybean acids				75·3	78·3
Polyallyl alcohol					
units per mole	9·5	8	16·5	9·5	16·5
% excess	8·8	11·9	9	8·8	9
Properties of ester					
Acid value	1·5	4·3	11·1	2·4	11·7
Colour (Gardner)	9–10	9–10	11–12	10	8–9
Visc. (Stokes)	4·2	5·2	40·8	4·7	19·5
Gel time (min.)	33	31	1	62	—
Set time (h)†	2	$1\frac{3}{4}$	$\frac{3}{4}$	3	$1\frac{1}{4}$

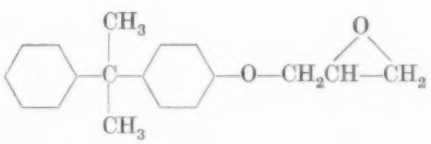
* According to Cox, Jerabek and Konen (1953).
† With 0·2% Pb and 0·025% Co as naphthenate.

with maleic resins. Ageing caused film embrittlement which is a characteristic of nitrogen-containing compounds. Because of relatively high cost and limited availability of such amino alcohols, they were not extensively promoted.

Epichlorohydrin–bisphenol resins. Epichlorohydrin–bisphenol resins are considered in this section because they can be used as polyols in the preparation of protective coating materials. They form ester type products by reaction with fatty and resinous acids, or reaction with glyceride oils.

The epoxy, or 'Epon' resins, are prepared by the reaction of a bifunctional phenol, sodium hydroxide, and epichlorohydrin. Their structure is as follows:





The epoxy resins as we know them today, are the results of an intensive study by Greenlee (1944, 1950, 1951, 1952), whose work is covered in a number of patents, concerning both the use and preparation of these products. The first resins of this family were prepared as early as 1940. Raw materials were lacking at that time but they were considered a definite post-war possibility. Since the end of the war material building blocks of these resins have become available in sufficient supply to meet the demand. The first epoxy resins

appeared on the market in about 1945 in very limited amounts. Their use has increased rapidly to the present rate (1954) of 30,000,000 lb per year (ANON, 1954a).

The epoxy resins vary in melting point as a function of the number of units expressed by '*n*' in the above formula. The magnitude of '*n*' determines the number of esterifiable hydroxyl groups, which can vary from 4 to 40. The esterification reactions can take place by the opening of an epoxide ring to form an ester–hydroxy configuration which can be esterified further with fatty or resinous acids.

The use of epoxy resins is not limited to reactions with fatty acids alone. RINSE (1953) describes a method for preparing resinous oil products by reacting epoxy resins and oils of the linseed and soybean types.

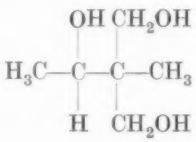
Enamels and varnishes based on these resins are available commercially. They have good durability and weathering characteristics and show excellent alkali- and water-resistance in either clear or pigmented coatings. Because of the high functionality of these resins even the oleic acid esterification product dries to a film possessing good alkali-resistance.

These resins also find use in other fields such as potting compounds, laminates, pipe materials and similar items. In such instances they are cured by reaction with diamines, e.g. diphenylene diamine (SHELL CHEMICAL CORP., 1952).

Miscellaneous polyols. Several methods are described to increase the functionality of glycerol and pentaerythritol. WITTCOFF and ROACH (1951b, ROACH and WITTCOFF, 1950, 1951) prepared ether alcohols by reacting glycerol, pentaerythritol, allyl alcohol and allyl ethers with glycerol monochlorohydrin in the presence of sodium hydroxide. Polyols of similar nature have been prepared by ZECH (1951, 1952) who reacted glycerol with epichlorohydrin employing borontrifluoride as a catalyst. Esters with fatty acids and phthalic anhydride are described by WITTCOFF and ROACH (1951b, ROACH and WITTCOFF, 1950, 1951).

Variations of these reactions have also been patented (WITTCOFF and ROACH, 1950a, 1951a,b and other oil and wax-like materials have also been described (WITTCOFF and ROACH, 1950b).

The preparation of 3,3-dimethylol-butanol-2 from methyl-ethyl ketone and formaldehyde has been described by Wuellenweber (ANON., 1953)



The reaction is analogous to that used in the pentaerythritol preparation.

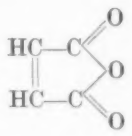
Exceedingly high molecular weight alcohols and their drying oil esters have been prepared by WAYNE (1951). Ethylene is treated with carbon monoxide to form polyols with a molecular weight of 1,900.

IV. Modification by Alpha–beta Unsaturated Acids

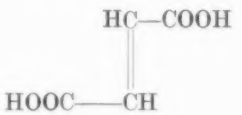
A. Modification by adduct formation

Several α–β unsaturated mono- and di-carboxylic compounds have found wide use in protective coating materials. These compounds include the following acids or anhydrides listed in the order of importance:

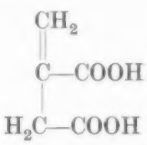
Maleic anhydride



Fumaric acid

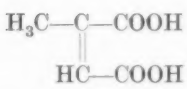


Itaconic acid



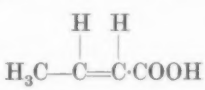
and

Citraconic acid



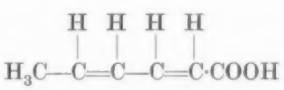
Definitely less important, from the standpoint of adduct formation, are

Crotonic acid



and

Sorbic acid



Maleic anhydride is the most widely used in the field of oil and resin modification for use in protective coatings, printing inks and lacquers.

1. *Maleic anhydride*

Use of maleic anhydride for oil modification dates back to the German patent of Springer and Möller A.G.* in 1936. Linseed and poppyseed oils were reacted with maleic anhydride and then esterified with glycerol. Prior to this time it was thought that only oils with conjugated unsaturation would react with maleic anhydride thus forming a Diels–Alder type adduct. Beavan and Tervet (1939) were granted a series of British patents showing that oils which do not contain conjugated unsaturation such as linseed and soybean, will react with maleic anhydride to form products useful as plasticizers for

* Dr. Christian Möller-Lobeck was the inventor.

nitrocellulose lacquers and raw materials for varnishes. They also point out that these adducts can be esterified with polyhydric alcohols. This was followed by a series of patents by CLOCKER* in 1940 which showed that maleic anhydride adducts of non-conjugated oils can serve as intermediates for a number of oil based products.

The most important derivatives in these three groups of patents concern the esterification of the maleic adducts with polyhydric alcohols. These products find a wide range of uses depending upon the base oil, degree of maleic modification, (usually expressed as percent based upon the oil) and polyol used to neutralize the acidity. Numerous review articles on the maleic modified oils have appeared (BALTES, 1950; BEVAN, 1943; HUNDERT, 1952; KAPPELMEIER and VAN DER NEUT, 1950; TERRILL. 1953a).

Maleic anhydride will react with non-conjugated acids at approximately the following temperatures: (a) linolenic acid, 160°C; (b) linoleic acid, 165°C; and (c) oleic acid, 190–200°C. There are two primary methods for preparation of maleic treated oils: (a) reaction of oil with maleic anhydride and then a polyhydric alcohol, and (b) partial alcoholysis of oil with a polyhydric alcohol followed by addition of maleic anhydride. (This simultaneously esterifies the alcoholysis product and reacts with the oil unsaturation.)

At the present time the second method has wider application. A process typical of the second method is described by ULLMANN *et al.* (1952) and SCHWARCMAN (1946). According to these patents an oil is alcoholised with a polyhydric alcohol, e.g. glycerol, using litharge as a catalyst. Either fumaric acid or maleic anhydride is added to this product and the reaction is brought to completion. MOORE (1949) described a somewhat similar process in which a monoglyceride is reacted with maleic anhydride. RUST (1950) prepared a series of partial pentaerythritol esters of tall oil and then reacted these with maleic anhydride or a partial ester of maleic acid.

Air and peroxides have been suggested as catalysts for maleic anhydride addition. (ROOT, 1945) describes the use of benzoyl peroxide catalyst. Under these conditions the reaction takes place at a much lower temperature, i.e. 110°C as compared with 160–190°C without a catalyst. The resultant product is more viscous than that prepared at the higher temperatures. However, varnishes prepared from these oils do not differ in physical characteristics and performances (RHEINECK, unpublished) from those made from uncatalysed reaction products. The initial constants are somewhat different from oils prepared according to the Clocker process.

PLIMMER and ROBINSON (1944) and TAYLOR and SMULL (1936) showed that blown oils will react quite readily with maleic anhydride. This may be caused by the presence of peroxide groups in the blown oil molecule. CHARLTON *et al.* (1944) found that a reaction would take place between maleic anhydride and linseed oil by using half esters of the former and blowing air through the reaction mixture.

Strong acids of a sulphonic acid type were suggested by RUST (1942) as

* The application date of the basic Clocker patent is 1934, thus pre-dating the Springer and Möller patent.

catalysts for expediting the reaction at somewhat lower temperatures. The use of catalysts has not generally been accepted. There is no advantage to be gained on a performance basis.

Mono- or di-esters of maleic acid will react in a manner similar to maleic anhydride. RUST (1949, 1951b) describes the use of both monoallyl maleate and diallyl maleate as the additives. Methallyl esters (IMPERIAL CHEMICAL INDUSTRIES, 1943) have also been used. SORENSON (1942) describes the use of similar esters for the improvement of the oil but uses benzoyl peroxide as a catalyst.

The colours of the maleic anhydride oil adducts, are generally about the same as the base oils. KOSMIN (1951) claims the colour can be improved by running the reaction in the presence of boric acid. Alkaline compounds degrade the colour.

There has not been much incentive to react conjugated oils such as China wood or oiticica with maleic anhydride, although MORRELL *et al.* (1934) describe the use of this adduct to prepare heat-convertible oils which are thermosetting. Technically, no distinct advantages are gained in maleinizing conjugated oils.

Especially useful linseed oil adducts have been prepared by both of the common methods. With 5–8 per cent maleic modification an excellent varnish oil is produced which serves as a China wood oil replacement. Soybean oil modified with about 6–7 per cent maleic anhydride can be made to perform in a manner equivalent to dehydrated castor oil in oleoresinous varnish systems. Soybean oil of lower maleic modification can be used as a replacement for linseed oil in house paints (FLETT *et al.*, 1953). The durability of such oils generally approaches that of a linseed oil.

GUTKIN (1951) evaluated the varnish performance of fish, linseed and other oils, treated with maleic anhydride. These data show an equivalence in the performance of the various types of oils but unfortunately do not indicate the degree of modification with the anhydride.

Maleic anhydride has found its greatest use in the upgrading of oleoresinous systems, comprising oil, rosin and polyhydric alcohol. It is claimed by SCOTT (1947) that the simultaneous reaction of the above-mentioned ingredients yields varnishes possessing properties superior to those made in any other way. COHEN *et al.* (1945) claimed that a product made by co-reacting soybean oil, rosin and maleic anhydride followed by esterification made a harder print paint for linoleum than the corresponding product made from oil and a hard maleated resin. RUST (1946) describes the preparation of a varnish material made by reacting a glycerol or pentaerythritol rosin ester with mono- and di-allyl maleates followed by reaction with a drying oil.

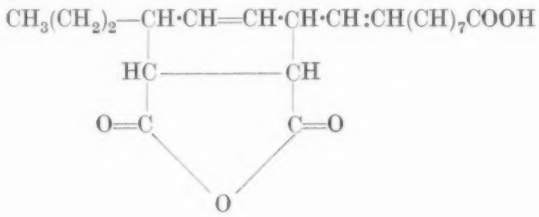
Maleinized oils, e.g. linseed and soybean, have found use as a base for copolymer-type vehicles. *cyclo*Pentadiene copolymers of this type patented by GERHART and ADAMS (1946, 1948) are discussed under 'copolymers'.

Oil-maleic adducts also serve as a starting material for other types of reactions. EILERMAN (1947, 1948) describes the use of water or steam to open the anhydride structure followed by neutralization with sodium silicate and dispersion in

28 per cent ammonia. This product can be applied as a water-based material which dries to a water-insoluble film. Maleic anhydride adducts of both conjugated and unconjugated oils have been treated with basic compounds, i.e. amines and ammonia, to prepare water-dispersible vehicles. CLOCKER (1940) used ammonia. Rust inhibitors and lubricating-oil additives have been prepared by BLAIR (1947a) by reaction of the maleic adducts of China wood and soybean oils with amines to form amides or imides. BLAIR (1947b,c) describes also the reaction of these products with ethylene oxide.

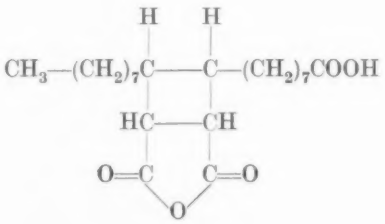
BOLLEY (1947) claims that a better water-based paint can be prepared if the oil contains a higher percentage of maleic anhydride. He describes the preparation of an oil from dehydrated castor and linseed treated with 6 per cent of maleic anhydride.

Considerable effort has been expended in various countries to elucidate the nature of the maleic anhydride addition reaction. In the case of conjugated oil systems, MORRELL and SAMUEL (1932) showed that it was a diene addition. China wood and oiticica oils and conjugated oil fatty acids were considered in this study. The reaction product is a typical Diels–Alder 1–4 adduct:



I

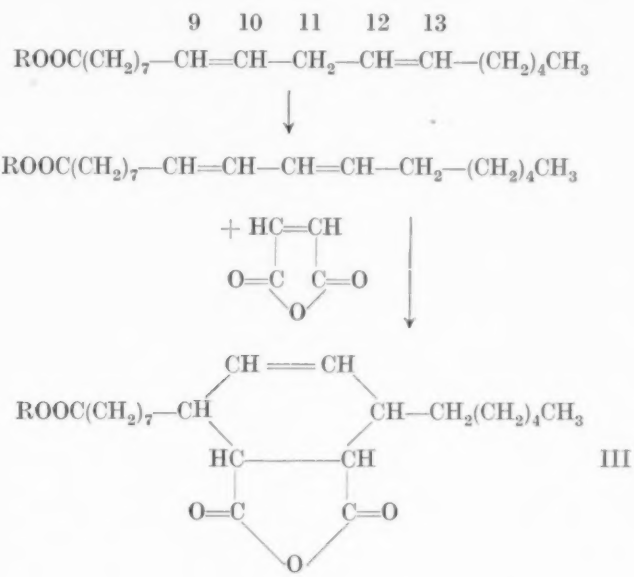
In the case of non-conjugated oils the determination of the structure of the adduct has been more difficult. Structural information was indefinite for a long time, but this did not forestall the preparation and use of maleated oils. Thus, the patents of SPRINGER and MÖLLER (1936) and BEVAN and TERVET (1939) admittedly make no attempt to define the nature of the reaction. CLOCKER (1940) postulated a *cyclo*butane structure for the oleic acid adduct:



II

In the case of polyunsaturated acids, a 1–4 diene (Diels–Alder) addition similar to that discussed above (see I) for conjugated oils has been suggested. It is assumed that reaction is preceded by a shift from the non-conjugated to

conjugated forms. If maleic anhydride is present it can react to form a Diels–Alder adduct which in the case of linoleic esters occurs as follows:



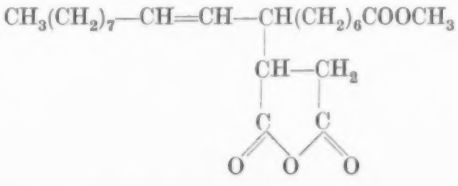
III

High temperatures favour the conjugated structure.

The formation of a substituted succinic type adduct is also possible for maleated oils. It is this structure which is considered by oil chemists to predominate in preference to the Diels–Alder adduct, although the presence of a small amount of the latter has not been excluded. Support for the succinic type structure has been obtained by Bickford *et al.* (1942, 1948); Teeter *et al.* (1948), and Kappelmeier and van der Neut (1950). Reactions of maleic anhydride with pure methyl oleate, methyl linoleate and methyl linolenate were studied. From this work it appears that a hydrogen on a carbon atom α to a double bond becomes activated to form a compound of the succinic type with maleic anhydride.

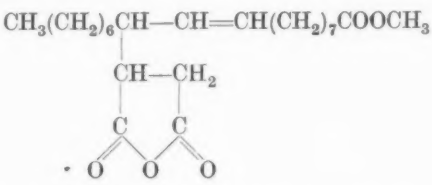
The structures suggested in the succeeding formulae are based upon suggestions of the above groups of investigators. Addition to oleic acid may occur at the eighth carbon atom.

The adduct of oleic acid may be as follows:



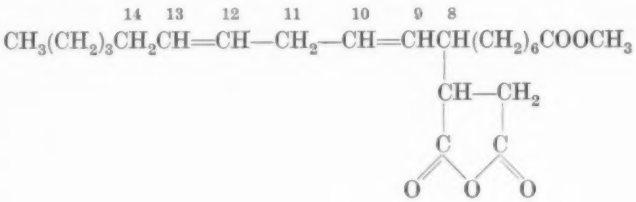
IVa

or at the eleventh carbon atom,

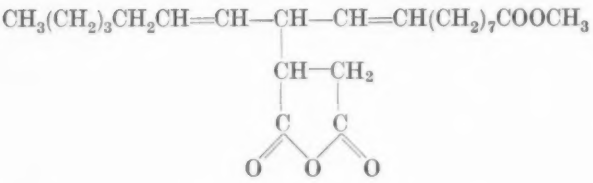


IVb

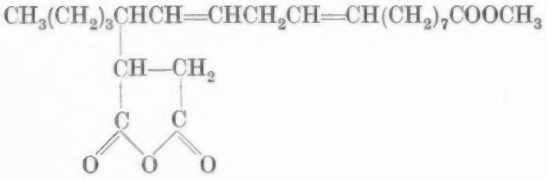
With methyl linoleate three simple succinic-type adducts are postulated with reaction occurring at the 8, 11, or 14 carbon atoms. Of these the methylene at the 11 position is probably favoured (Vb)



Va

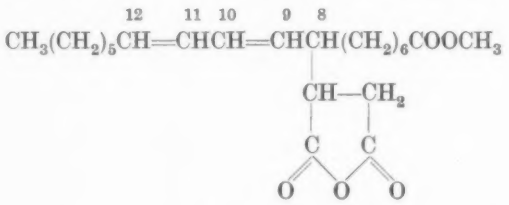


Vb



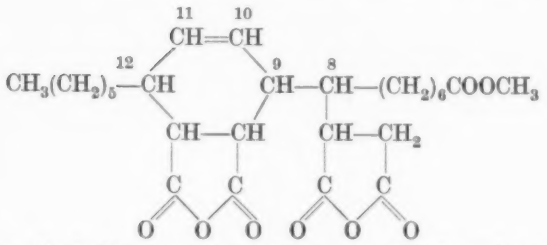
Vc

It is postulated by KAPPELMEIER and VAN DEN NEUT (1950) that conjugation may occur simultaneously with attack at a methylene carbon, or that the initial adduct such as Va or Vc may rearrange to the conjugated structure as follows:



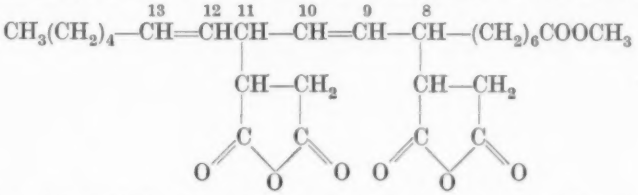
VI

Diels–Alder addition of a second mole of maleic anhydride to the conjugated structure would give:



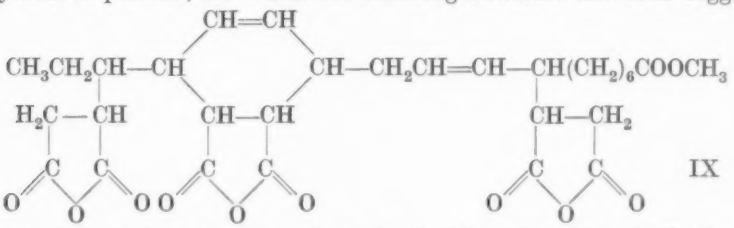
VII

Alternatively the unconjugated structures Va, b, and c may add a second mole of maleic anhydride at a methylene carbon to give a structure such as:



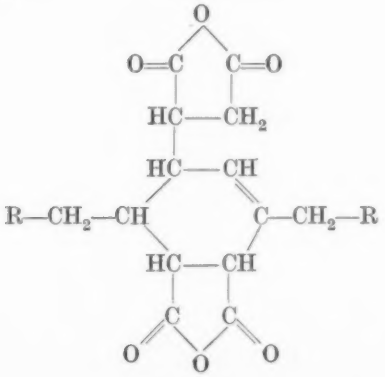
VIII

With linolenic acid the first adduct possesses a structure analogous to those of IV or V. A second addition probably gives structures analogous to VIII or, if conjugation takes place, to VII. Introduction of a third mole of maleic anhydride is possible, for which the following structure has been suggested:



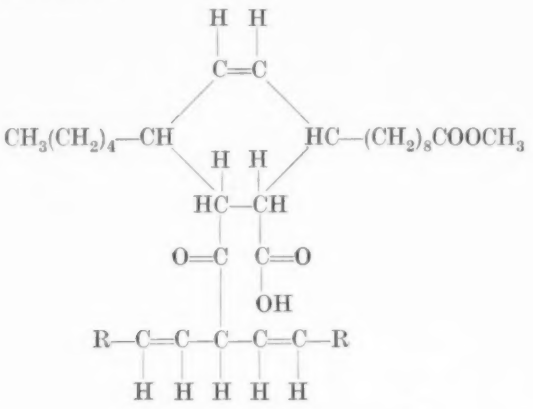
IX

In addition to the structures shown by V, VI, VII, VIII and IX, PLIMMER (1949) believes that the second maleic anhydride can add to the opposite side of the hexene ring in the Diels–Alder type adduct shown in structure I or Ia to form the following:



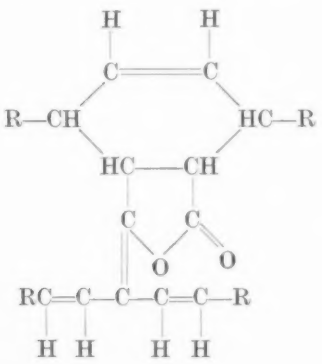
X

Based on differences in acid and saponification values, PLIMMER also postulates a second type of structure, in which the maleic residue acts as a bridge between two acids chains. The Diels–Alder adduct (structure I) reacts further as shown in XI and XII as follows:



XI

This ketone, XI, enolizes and forms a lactone, thus;



XII

The conclusions of PLIMMER appear to be justified by his analyses. It has been observed frequently that the saponification values of maleated oil products do not agree with what would be expected from the original fatty esters and maleic anhydride. It has recently been shown by SHAW and FORMO (1954) that saponification values agreeing substantially with the theoretical for maleated oils result if butanol is used in place of ethanol in this determination. In light of this more recent work it appears the existence of compounds conforming to structures X, XI and XII is questionable.

According to FLETT *et al.* (1953), the succinic type adduct such as IV, V and VIII predominates over types represented by VI, VII and IX.

The work to establish the identity of the various adducts described above was performed with higher percentages of maleic anhydride than are used in the

maleated oils of commerce. Most maleic additives do not exceed about 8 per cent. This means that for 1 mole of drying oil (mol. wt. ca. 870) about 70 g of anhydride would be required for an 8 per cent modification. This is equivalent to about 0·72 mole of maleic anhydride for each mole of oil, or, for 3 moles of fatty acid in triglyceride form.

It is believed that the most highly unsaturated acids react first. Hence, in linseed oil (cf. Table 5) with 51 per cent linolenic and 17 per cent linoleic acids, it would be expected that monosuccinic derivatives of linolenic acid would form first by reaction at the 11 or 14 carbon atoms (or, less likely, at the 8 or 14 carbon atoms). In soybean oil (cf. Table 5) with 5 per cent linolenic and 54 per cent linoleic acids similar types of addition would be expected. Addition of a second mole of maleic anhydride in the same chain would be unlikely.

The products formed are polybasic acids. Esterification with polyols yields products of increased functionality and complexity.

2. *Fumaric acid*

Fumaric acid is the second most important α-β unsaturated acid for oil upgrading. Although its possibilities have been known for a long time (Rheineck, unpublished) it has not been available in adequate supply and at sufficiently low price to encourage its use until recently. Fumaric acid can be used with oils in methods and processes analogous to those described for maleic anhydride on a mole for mole equivalence. Some technologists assume this on a pound for pound equivalence, but on a stoichiometric basis, the percentage of fumaric modification is slightly higher than with maleic.

Grummitt (1954) claims that reaction of fumaric acid and oil can be catalyzed by the addition of between 0·1 and 2 per cent of free halogen, e.g. iodine. It is possible that under these circumstances the iodine catalyses the isomerization of the oil to a conjugated system with which the fumaric acid can readily react.

The fumaric and maleic oil adducts appear to be equivalent, with initial colour and colour stability in favor of the former. Colour advantages are especially true in the case of heat-bodied oils. The heat bodying rates and Sanderson dry times of equivalently modified oils are indistinguishable.

Fumaric acid modified oils are especially useful in the preparation of interior white enamel vehicles, even when based on linseed oil, and seem to have properties quite similar to those based on soybean oil with respect to non-yellowing characteristics.

3. *Citraconic and itaconic anhydrides*

Citraconic and itaconic anhydrides have also been investigated as upgraders. Teeter, *et al.* (1949) have described a series of reaction products of methyl linoleate with itaconic and citraconic anhydrides. They separated the various adducts via reaction with ethylene diamine. The monoadduct gave a tacky resin; the diadduct yielded a gel.

Haines and Bilello (1951) point out that itaconic acid will give a lower-viscosity oil than either maleic or fumaric acid at a given acid value. Itaconic-acid-modified oils body more slowly, and hence more of the acid can be used. They state that modification of soybean oil with 20 per cent of itaconic acid gives properties about equivalent to 10 per cent of fumaric acid.

Citraconic and itaconic acids have not been used to any great extent in the modification of oils because of their unavailability and excessive cost as compared with either maleic or fumaric acids.

Alpha-beta unsaturated monobasic esters form adducts similar to those of the maleic type dibasic acids and esters. Teeter *et al.* (1946) reacted ethyl crotonate and crotonic nitrile with nickel isomerized methyl linolenate. The various adducts were found to be compatible with cellulosic film formers.

B. Esterification with short-chain unsaturated monobasic acids

One of the methods used to gain functionality in a glyceride oil molecule involves synthesis of co-esters of linseed and soybean acids with short-chain unsaturated acids. The term 'short-chain acids' is used here to cover a large variety of unsaturated, variously substituted compounds with not more than about 10 carbon atoms. A method for esterification is described in Agre (1945).

The simplest acids in this series are acrylic and methacrylic. They are difficult to co-esterify with fatty acids to yield a synthetic oil. Hewitt and Armitage (1948) succeeded in esterifying a diglyceride with methacrylic acid in the presence of a solvent. Methacrylic anhydride (DuPont de Nemours, 1939) has also been used. A substituted acrylic acid, such as β-furyl acrylic acid has been esterified by Rothrock (1945b) to produce oils and resins (1945c).

The most widely investigated unsaturated acid of the series is sorbic acid, hexadien-2,4-oic acid. Cupery (1945b) described the linseed co-esters. Tall oil mixed sorbic esters are described by Barthel (1949). Schector (1951) claims that castor oil treated with sorbic acid acquires properties like China wood oil.

Hexadienoic acid became available immediately after World War II as an upgrader, and it is the most important of the acids discussed in this section. Its use is described in a bulletin (Carbide and Carbon Chemical Corp., 1946). It was recommended that an oil such as linseed be alcoholized with glycerol and basic catalyst. The alcoholysis product is then esterified with a quantity of sorbic acid equivalent to the added polyhydric alcohol.

Sorbic acid modified oils dry faster to give harder films (Archer-Daniels-Midland, unpublished) than the glycerides but show poorer drying qualities than equivalent maleic modified oils. Indications are that a linseed oil modified with about 5 per cent of maleic anhydride and esterified with glycerol yields film characteristics equivalent to a linseed oil modified with about 11·3 per cent of a corresponding sorbic ester. Also, with soybean oil, 5 per cent maleic anhydride modification esterified with glycerol is the equivalent of 15½ per cent sorbic acid modification. Varnish cooking procedures showed that oils of the sorbic types are somewhat inferior in speed of cooking and colour to maleic oils.

A sorbic-acid-modified soybean oil for house paints shows inferior flow and gloss when compared to the corresponding maleic-treated oil.

It was also shown by CUPERY (1945b), that soybean oil modified with 5 per cent sorbic acid is equivalent to linseed oil. Similarly, linseed oil modified with 15 per cent sorbic acid is equivalent to dehydrated castor oil. With higher modifications linseed oil attains properties like those of China wood oil.

SCHECTOR (1951) and TURKINGTON *et al.* (1950) investigated hexadienoic acid modified oils in oleoresinous systems, using rosin, maleic anhydride and fatty acids. A linoleum base made by dispersing a gelled hexadienoic co-ester in rosin was suggested by CUPERY (1945a).

The general conclusions from those who have investigated the upgrading of oils with sorbic acid seems to be that an equivalent improvement can be obtained at considerably less cost by using maleic anhydride as a modifying agent.

Table 14. *Some typical short-chain unsaturated acids used to modify oils*

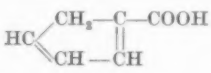
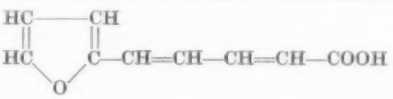
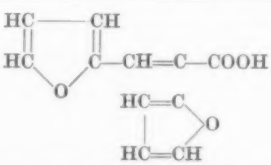
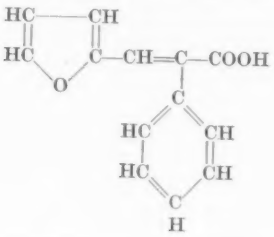
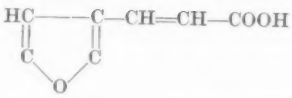
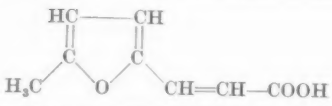
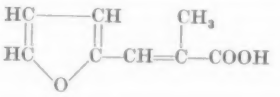
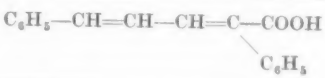
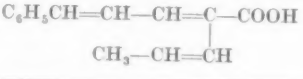
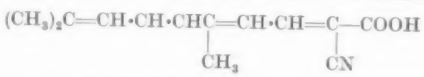
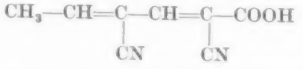
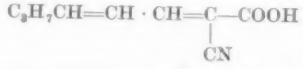
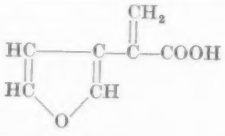
Name	*Formula*	*Reference*
Acrylic acid	$H_2C{=}CH{-}COOH$	
Methacrylic acid	$H_2C{=}C(CH_3){-}COOH$	HEWITT and ARMITAGE (1948)
2,4-hexadienoic acid (Sorbic acid)	$CH_3CH{=}CH{\cdot}CH{=}CH{\cdot}COOH$	CUPERY (1945b) BARTHEL (1949)
Octatrien-2,4,6-oic acid	$CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}COOH$	CUPERY (1945b)
7-phenyl heptatrien-2,4,6-oic acid	$C_6H_5{\cdot}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}COOH$	CUPERY (1945b)
1,3 *cyclo*pentadiene carboxylic acid		CUPERY (1945b)
5-(α-furyl) penta-dienoic-2,4-oic acid		CUPERY (1945b)
α,β-di(α-furyl) acrylic acid		ROTHROCK (1945c)

Table 14—*continued*

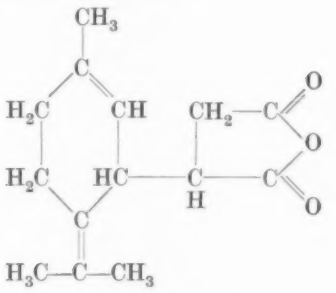
α-phenyl,β-(α-furyl) acrylic acid		Rothrock (1945c)
β-(β-furyl) acrylic acid		Agre (1945) Rothrock (1945b, c)
β (α-(α-methyl furyl) acrylic acid		Rothrock (1945c)
α-methyl-β-(α-furyl) acrylic acid		Rothrock (1945b)
2,5 diphenyl pentadien-2,4-oic acid		Brubaker (1945a)
5-phenyl 2-(propene 1) pentadiene-2, 4-oic acid		Brubaker (1945a)
2-cyano-5,9-dimethyl decatrien-2,4,8-oic acid		Cupery (1945b)
2,4-dicyano-hexadien-2,4,oic acid		Cupery (1945b)
2-cyano-octadien-2-4-oic acid		Cupery (1945b)
α-(β-furyl) acrylic acid		Rothrock (1945c)

A number of other acids have also been investigated. Structures of some are shown in Table 14. SAUER (1945) DUPONT DE NEMOURS (1947) listed the co-esters of a series of α-β ethylenic-α (or β)aryl, monocarboxylic acids. Alpha-cyano substituted acids with double bonds in the 2 and 4 position are described by CUPERY (1945c). Aromatic substituted cinnamal-acetic acid co-esters are disclosed by ERUBAKER (1945) in which the double bonds are in the 2 and 4 position with the phenyl group on the end of the chain or α to the carboxyl. Alpha-beta ethylenic α-alkenyl-1-mono acids as upgraders are described by SAUER (1945) and DUPONT DE NEMOURS (1942a). In this instance, a vinyl group is α to the carboxyl in a cinnamic acid. Somewhat similar acids are also described by CUPERY (126b) as acyl-acrylic acids. Substituted benzoic acid esters of glycerol are disclosed by CUPERY (1948), specifically, *p*-cinnamoylbenzoic acid co-esters. BRUBAKER (1945b) described the co-ester of thienyl acrylic acids which include those with double bonds in the α-β position and thienyl groups at either carbon atom.

The above acids have been tried as oil modifiers in a manner similar to that described for sorbic acid. None has been used commercially.

Miscellaneous products

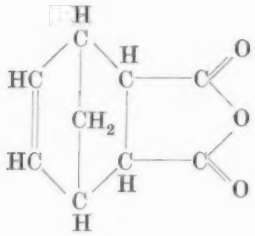
A group of dibasic acids can be prepared by treating maleic anhydride with terpenes, conjugated dienes and olefins. Terpinolene, pinenes, limonene, and related terpenes react with maleic anhydride to form 'Petrex acids'.* One or more maleic residue may be incorporated in the final product. The terpinolene monoadduct has the following configuration:



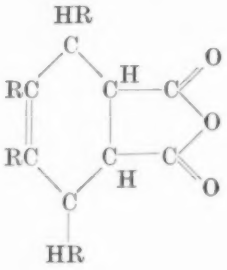
In a given ester composition, the 'Petrex acids' are more effective than phthalic anhydride in promoting gelation. On this basis about 0·6–0·65 mole of the former is equivalent to 1 mole of the latter.

Olefins yield several varieties of acids. The Diels–Alder adduct of *cyclo*-pentadiene and maleic anhydride is marketed as 'Carbic anhydride'† or 'Nadic anhydride'.‡

* Hercules Powder Co.
† Bakelite Corp.
‡ National Aniline Division, Allied Chemical and Dye.



Other dienes, e.g. butadiene, isoprene, and homologues, yield partially hydrogenated or substituted phthalic anhydride types (R is either a hydrogen or alkyl radical).



Both the terpene and olefin maleic adducts are more reactive with oil than phthalic anhydride. According to Cosgrove and Earhart (1949) they react more like maleic anhydride and are probably maleic carriers.

An '*in situ*' method for reacting di*cyclo*pentadiene with maleic anhydride in the presence of oils to yield alkyd resins is described by Gerhart and Adams (1947).

Lane and Parker (1948) found that fumaric acid will also react with dienes to form adducts. The use of these in coating compositions is disclosed.

Myers and Muckerheide (1948) state that an oil can be upgraded by replacing the saturated acids with azelaic acid via an acidolysis reaction. The reaction is conducted under vacuum and is especially beneficial with sardine oil.

Recently, Elwell (1953) showed that an oil could be modified by alcoholysis with a polyol followed by esterification with a tetrabasic acid, e.g. pyromellitic. This acid is made by reacting maleic anhydride with 1,2-dihydrophthalic acid.

Dibasic acids have also been prepared by dimerizing fatty acids. These are discussed under the 'Norepol' process.

V. Separation of Non-drying and Drying Components

Naturally occurring oils contain appreciable quantities of non-drying constituents. Numerous attempts have been made to separate these from components which have drying properties. Both physical and chemical methods have been tried but the former generally have been preferred for economic reasons.

A. Solvent separation of fatty acids

BROWN and SHINOWARA (1938) showed that the fatty acids in a four-component system containing saturated, oleic, linoleic and linolenic acids could be separated by crystallization at low temperatures. In this work it was found that the saturated fraction can be removed at 0 to −10°C. Oleic acid will crystallize at −20°C, linoleic acid at −45°C, and linolenic acid at −75°C. The solutions used in this work were much too dilute to be practical. BOLLEY (1944) and SCHLENKER (1952) also describe low-temperature fractionation processes. BROWN and KALB have reviewed the methods of segregation of fatty acids and esters by low temperature crystallization in Chapter 3, Vol. 3 of this series.

Successful separation by the solvent crystallization process demands that the fatty acids be obtained in a readily filterable form. This end has been achieved by MEYERS and MUCKERHEIDE (1943) and has been further developed into the 'Emersol process' described by DENMERLE (1947). The novelty of this process lies in the use of a solvent such as acetone, ethanol or methanol containing up to 15 per cent of water. Sometimes a crystal promoter, such as a fat derived from one of the acids, is used to produce crystals of the proper size when the solution is chilled to 10°C. The 'Emersol process' is now an established method. Typical data on acids separated by this process are shown in Table 15.

Table 15. *Typical separations of acids by the Emersol process**

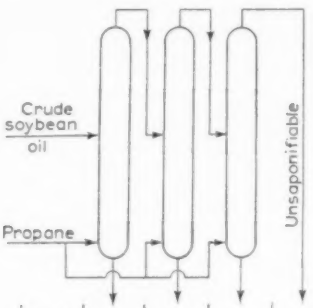
Base material			*Separation products*			
Fat	*Titre* °C	*Iodine value*	*Acid products*	*Yield* (%)	*Titre* °C	*Iodine value*
No. 1 tallow	42·4	52·2	Stearic	51	54·2	6·0
			Oleic	49	2·0	—
Yellow grease	45·2	44·7	Stearic	52	54·2	6·0
				48	2·0	
Linseed oil	—	185·0	Solid	14	44·7	87·0
			Liquid	86	—	195·0
Soybean oil	—	129·3	Solid	15	48·5	50·0
			Liquid	86	—	144·0
Sardine oil	—	160·0	Solid	25	—	30·0
			Liquid	75	—	201·0

* According to DENMERLE (1947).

Other processes using a similar principle are also described. Thus, GEE (1950) used equal volumes of soybean acids and acetone, chilled to about 2°C. SPANNUTH (1950) showed that fatty acids could be quite satisfactorily separated into two fractions by crystallization from hexane solution using careful temperature control. FELDPUSH (1950) disclosed that a mixture of solvent and liquid fatty acids chilled to −5°C and −15°C could be treated with a solvent in such a fashion that the more highly unsaturated acids would leach out.

B. Solvent separation of oils

Hixson and co-workers (Drew and Hixson, 1944; Hixson and Hixson, 1941; Hixson and Bockelman, 1942) found that high-molecular weight fatty acids or their esters could be separated in propane at high temperatures approaching the critical temperature. Liquid propane under pressure and a number of other normally gaseous hydrocarbons of low molecular weight readily dissolve fats and oils at ordinary temperatures. If the solution is heated there is an abrupt



Fraction	Crude	I	II	III	IV
Yield %	–	2	25	72	1
Colour–Lovibond	75Y	–	75Y	25Y	–
	25R	–	8R	25R	–
Iodine values	135	100	135	128	115
Free fatty acids	0·4	5·0	0·02	0·04	20
Unsaponifiable	0·9	2·5	0·3	0·3	60
Saponification No.	192	190	192	192	80

Fig. 7. Typical flow Diagram and results of soybean oil fractionated by the Solexol process. According to Passino (1949).

transition point with separation into an oil-rich, solvent-poor fraction and a solvent-rich, oil-poor fraction. There is segregation of oil components between the two fractions. Composition varies with temperature. This work was a basis of the 'Solexol' process described by Passino (1949) and Hixson and Miller (1953). In this process, oils are treated with liquified hydrocarbon such as propane in a continuous counter-current extraction system at definite temperature and pressure conditions. After contact, two immiscible liquid phases differing in density are formed. The less dense liquid contains the more saturated glycerides and the more dense fraction contains the more unsaturated glycerides. By operating in a column of good efficiency, practical separations can be accomplished as shown in the flow diagram in Fig. 7. The process is especially beneficial in segregating fish oils.

le Richie and Stubbs (1954) describe in detail the various fractions which can be obtained by the 'Solexol' process both on a theoretical and practical basis from soybean, tobacco seed, dehydrated castor and fish oils. For instance, they segregated a South African pilchard oil with an iodine value of 195 into three fractions, namely, 5 per cent with an iodine value of 240, 80 per cent with an iodine value of 205, and 15 per cent with an iodine value of 130.

In addition to separating the oils on the basis of unsaturation, the process also segregates the colour bodies into the more highly unsaturated fractions and thereby refines the other fractions. Fatty acids also can be largely removed from the major fractions.

Chatfield (1953) showed that varnishes made from segregated Pilchard oils by the 'Solexol' process body faster and show greater reactivity with oil reactive resins than the unsegregated oil. The oils in themselves also dry much better than would be expected on the basis of iodine value alone.

Another method which has been used for the separation of components of oils and fatty acids having varying degrees of saturation has been the furfural extraction technique, developed by Freeman (1940, 1943, 1951).

Cooling of a furfural solution of an oil gives phase separation into a furfural-rich and a furfural-poor fraction. The oils in the two fractions vary in unsaturation. Naphtha may be used with furfural to improve the separation. In this process, soybean oil with an iodine value of 136·5 can be separated into an extract and raffinate with iodine values of 155 and 110 respectively. Proportionately similar enrichments in iodine values are obtainable with linseed and fish oils. The process is versatile and can be adapted to obtain wide variation in enriched unsaturated fraction.

The drying properties of oils enriched by this process exceed expectations based on iodine values (Rheineck, unpublished). A furfural-treated soybean oil extract with an iodine value of 158 dries faster and possesses less tack than an untreated linseed oil with an iodine value of 180. This improvement is partially caused by removal of minor oil constituents which may inhibit oil drying. The low-iodine-value raffinate contains many of the component glycerides containing one or two saturated acids.

The success of this process is dependent upon the market value of the low-iodine-value raffinate and unsaponifiable oil components. Removal of such non-drying glycerides or glyceride which can only form linear polymers disproportionately improves drying of the extract.

C. Separation of methyl esters

Methods for separating fatty acid esters of monohydric alcohols have also been described. A crystallization method (Armour & Co., 1953) has been used, and a solvent-extraction method has also been applied by Goss and Johnstone (1943).

D. Selective saponification of fatty acids

The various fatty acids in oils can be separated on the basis of soap solubility, and reactivity with bases. Thus, Buxton (1945) has shown that oils can be selectively saponified by using between 30 and 90 per cent of the alkali theoretically required to split the oil. The saturated glycerides are separated from the unsaponified fraction in the oil.

Nicholsen and Formo (1949) separated fatty acids into fractions of varying unsaturation by neutralizing with a mixture of sodium hydroxide and alkaline earth hydroxide using from 20 to 80 equivalent per cent of the alkaline earth

hydroxide in the mixture. The soaps so formed were separated and those which were more insoluble had the lowest iodine values. The more soluble soaps had the higher iodine values. Typical data from their work are shown in Table 16.

Table 16. *Segregation of soybean fatty acids* by preferential neutralization*†

Bases used				*Soluble acids*		*Insol. acids*
Alkali	*Equiv. %*	*Alkaline earth*	*Equiv. %*	*Yield %*	*Iod. val.*	*Iod. val.*‡
KOH	30	$Ba(OH)_2$	70	28	159·2	131·3
KOH	70	$Ba(OH)_2$	30	58	155·7	116·0
NaOH	30	$Ba(OH)_2$	70	11	156·8	137·0
NaOH	70	$Ba(OH)_2$	30	36	156·4	129·5
NaOH	30	$Ca(OH)_2$	70	8	143·9	139·5
NaOH	70	$Ca(OH)_2$	30	48	155·8	124·0
NaOH	30	$Sr(OH)_2$	70	28	161·9	130·2
NaOH	30	LiOH	70	22	162·5	132·8
NaOH	70	LiOH	30	56	152·2	122·5

* Original Iodine Value 139·2.
† According to NICHOLSEN and FORMO (1949).
‡ Calculated.

The saponification processes obviously have limitations in that soaps are necessarily formed first, which must be decomposed, and the fatty acids re-esterified to be of value.

E. Process for separation of tall oil.

As tall oil became more widely available it became important that the fatty and resin acid components of this material be separated for many applications. The methods other than the 'Solexol' process involved in separating the various components of tall oil have been more successful than those used in the separation of drying or semi-drying oil fatty acids.

GLYNN and HOFFERTH (1953) developed a process for fractionally distilling tall oil to obtain an overhead fraction consisting mainly of oleic and linoleic acids and a final fraction containing the resin acids. The process was further improved to remove the oleic acid and linoleic acid from the second fraction by crystallization techniques.

One of the processes normally used to determine the quantitative relationship of resin acids and fatty acids in a tall oil mixture consists in esterifying with methanol. Under normal esterification conditions only the fatty acids form methyl esters, whereas the resin acids remain unchanged. By titration with alkali the two components can be determined. A process related to this is described by DUNLAP *et al.* (1950) who esterified tall oil at a low temperature with a polyol such as pentaerythritol to completely form the fatty acid esters. Resin acids did not esterify at the low temperature of 180°C, and it was possible to separate them from the reaction mixture by extraction with naphtha.

A somewhat similar process is described by KOONCE and PERRY (1949) in which tall oil is selectively esterified with monohydric alcohols and the rosin removed on an adsorbant. After the two components are separated, the rosin is recovered by washing the adsorption medium.

According to ROSHER (1950) tall oil may be separated by selectively reacting the fatty acids first, and then the rosin acids with *cyclo*-hexylamine. After the two components have been separated the rosin-*cyclo*-hexylamine complex is decomposed with heat or mineral acids.

F. Directed inter-esterification

Many oils, such as fish and soybean oils, contain appreciable quantities of saturated fatty acid glycerides which detract from drying performance. These components can be removed by a process of inter-esterification resulting in an improved drying oil. The subject of interesterification has been reviewed by FORMO (1954).

The distribution of fatty acids in natural glycerides is selective rather than random. Fig. 8 shows the component glycerides at statistical distribution. In a simple sense, fats may be considered as composed of two acids, saturated

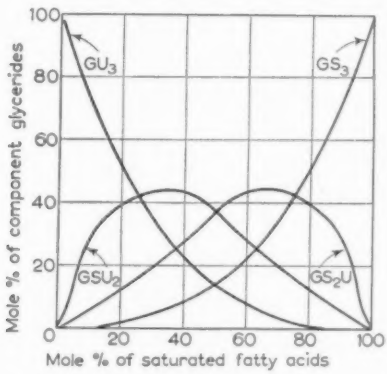


Fig. 8. Component glycerides at statistical distribution according to FORMO (1954). GU_3—triunsaturated; GS_3—trisaturated; GSU_2—monosaturated diunsaturated; GS_2U—disaturated monounsaturated.

and unsaturated. If the mole-fraction of saturated acids, S is s, and the mole-fraction of unsaturated acids, U is u, the composition of glyceride types is given by the following equations:

Trisaturated, $GS_3 = s^3 \times 100$ mole-per cent

Disaturated–monounsaturated, $GS_2U = 3s^2u \times 100$ mole-per cent

Monosaturated–diunsaturated $GSU_2 = 3su^2 \times 100$ mole-per cent

Triunsaturated, $GU_3 = u^3 \times 100$ mole-per cent

Normal fats and oils contain less trisaturated glycerides than would be predicted from Fig. 8. Inter-esterification to equilibrium gives the random or statistical distribution.

It has been shown by ECKEY (1948a,b) and WILLIAMS (1946) that a directed inter-esterification can take place in oils with a simultaneous crystallization of the trisaturated components. The liquid glyceride oil is treated with an alkaline catalyst, e.g. sodium alkoxide, sodium hydride or sodium metal. The catalyst and oil are cooled, and after a time, saturated glycerides, the least soluble components, separate. This upsets the equilibrium and more trisaturated glycerides form and gradually precipitate. The quantity which can be removed is a function of time and temperature. As an illustration, cottonseed and menhaden oils containing approximately 25 per cent of saturated acids will yield as much as 18 and 24 per cent respectively of the total acids in the form of saturated glycerides after standing with catalyst for about a week at 10°C. Separation gives a liquid fraction of much higher iodine value. If necessary a solvent can be used. The reaction is reversible, as is shown by the fact that the mixture will react again to give statistical distribution on warming if the catalyst is not destroyed with a small amount of acid prior to heating.

The potential value of the interesterification method for upgrading soybean and fish oils is considerable. Theoretically, on a mole basis 45–50 per cent of soybean oil consists of monounsaturated and diunsaturated glycerides which during drying can form only linear polymers. Removal of the saturated components improves drying characteristics by increasing the possibility of forming 'cross-linked' polymers.

Practical examples of the Eckey Process are reported by TOYAMA *et al.* (1953, TOYAMA and YAMAGUCHI, 1953) with peanut, rice bran, soybean, cuttlefish and sardine oils. YODA (1953) illustrated the effectiveness of this process in removing stearine from cuttlefish oil.

G. Other separation methods

A chromatographic method has been described by SWIFT *et al.* (1943) for the separation of methyl linoleate from other methyl esters. This method serves as a laboratory tool for separating various types of fatty acids with varying degrees of unsaturation. There is no commercial method based on this principle. Unsaturated and saturated fatty acids can be separated by the urea inclusion technique which has been reviewed by SCHLENK (1954).

VI. BODIED OILS

Less effort has been expended to improve the quality and processing of bodied oils than has been devoted to improvement of other vehicles. The trend is away from oleoresinous vehicles in favour of phthalic alkyd finishes and plastics. This section is a continuation of the review of the subject by RHEINECK in 1943.

Recent work on bodied oil improvement has centred on ways of improving drying properties by separating non-drying components from bodied non-conjugated oils such as linseed and soybean oils.

A. Removal of non-polymeric components

Solvent processes. Improvements in the use of solvents to segregate bodied oils are described by PRIVETT *et al.* (1947). They used acetone to segregate bodied oils into a series of reaction products varying in degree from non-polymeric to polymeric oil bodies. BERNSTEIN (1947) described the use of aliphatic alcohols having from 3 to 6 carbon atoms for a separation of bodied oil products. Other fractionation techniques have been described by WALKER and TAYLOR (1953) and RANSON and ZUCKER (1946).

Distillation methods. Work by MORSE (1941) on the distillation of bodied oils at 1 μ of mercury pressure, showed that the undistilled residue had improved properties. A similar technique was used to remove hormones, vitamins and the like from animal and vegetable oils (DISTILLATION PRODUCTS, 1941). The properties of the resulting oils were reviewed by EMBREE (1941).

With advancement in distillation processes, attempts have been made to separate the polymer portions from the non-polymer portions in oils by low-pressure short-path distillation. BARNITZ (1948) discloses a process in which a portion of the non-polymerizable components of the oil are removed prior to bodying and the bodied oil is again subjected to short path distillation. A process described by HICKMAN and BARNITZ (1952) is claimed to enrich a bodied soybean oil. In this case a yield of 55 per cent of distillate was recovered from the treated oil. A somewhat similar process is described by HARVEY and SCHAUFELBERGER (1945) in which bodied cottonseed and soybean oils were distilled under reduced pressure until about 35 per cent of the components were removed. Oils made by the above distillation processes are stated to have improved drying characteristics.

CARLETON (1945) has described a bodying process in which an ester interchange is used to concentrate the non-drying constituents in the same polyol ester. The non-drying components are in part hydrolysed by steam, and the pressure is adjusted to remove the liberated saturated acids by distillation. It is also pointed out that in this process the bodied oil polymerizes further.

The preparation of a 'super-bodied oil' in which steam is blown into an oil to a point just short of gelation is described by ARVIN (1952). The addition of steam seems to arrest the gelation reaction.

COWAN and AULT (1945) have described a process in which bodied oils are hydrolysed and converted to their methyl esters from which the non-polymeric material is distilled. Further reactions of the polymer with various other reagents are described. The technique is given in the description of the 'Norepol' process (p. 248).

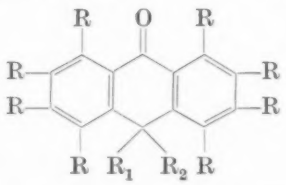
B. Bodying catalysts

The use of catalysts to increase the bodying rate of oils has attracted much interest. Many oil-bodying catalysts produce conjugation under proper conditions, although their effectiveness in oil bodying is not necessarily attributed to that mechanism. The catalysts used to produce conjugation, are considered in the section on isomerization.

Boron trifluoride complexes were used by BRADLEY (1951) and CROSTON *et al.* (1952) to body methyl esters and glycerides. KONEN and CLOCKER (1951) described a method for producing a gelled material by polymerizing a blown oil with boron trifluoride. The use of this catalyst in bodying oils has not been widely accepted because of its corrosive nature. Oils prepared in the presence of this catalyst have a tendency to continue to body if the catalyst's reaction is not properly arrested. Such means as the addition of water (BERGER *et al.* 1948) or a basic material will stop the reaction. BERGER *et al.* (1945) used quinoline to arrest the boron trifluoride reaction in oiticica oil. They also disclose the dispersion of the oiticica gels (1947) so prepared in unbodied oils for use as varnishes and undercoaters. PLANCK (1948) uses these gels to induce isomerization in non-conjugated oils with the aid of heat.

MOFFETT (1949) described the use of 3,4-epoxy-1-butene in linseed oil during the bodying reaction. It appears that this compound reacts with the acidity produced in the bodying process, and reduces the bodying time from 8 h to between 1 and 3 h.

PRATT (1950) used a complex formed from an olefin, e.g. ethylene, and sulphur dioxide, $C_2H_4SO_2$, as catalyst. KRONSTEIN (1952) indicated that bodied oils can be prepared in the presence of non-metallic peroxides. AUER (1946) used fluorescein. *p*-Anthrone and substituted anthrones have been described by PARKER (1954) as oil-bodying catalysts, These have the following structure:


R
O
R
R
R

Although most of the efforts have been focused on increasing bodying rates, certain treatments have been described to slow down the process. FRENCH (1949) stated that dodecyl mercaptan inhibited the gelation of both China wood oil and linseed oil. PARKER (1953) indicated that small amounts of compounds such as chloranil and trialkyl benzyl ammonium chloride will inhibit the gelation of polyester mixtures which are very prone to gelation.

VII. COPOLYMER OILS

Products in which an oil (natural, modified, or synthetic) is reacted with or in the presence of a second agent to form a homogeneous appearing complex are considered under this heading as 'copolymers'. This definition does not distinguish whether the copolymer is an actual chemical combination in a homogeneous system or whether it is a heterogeneous mixture of polymers mutually compatible with one another. The discussion in this section is limited largely to the reactions leading to copolymers of oils or their (monobasic) acids, followed by esterification, rather than systems prepared as alkyd resin products.

It has long been recognized that unsaturated oils will polymerize with themselves to form viscous bodies. It is also known that the other unsaturated compounds which are discussed in this section will polymerize with themselves to form products of increased viscosity with film forming properties. The problem is to effect polymerization and/or copolymerization of both oil and the other compounds to form a compatible system in both liquid and dried film states.

There have been a number of compounds proposed for copolymerization with oils of which styrene and *cyclo*pentadiene are of greatest importance. Other monomers such as isoprene, butadiene, hexadiene, acrylonitrile, alkylacrylates, etc. have limited importance.

A. Styrene–glyceride oil copolymers

Historical. Use of styrene for copolymerization with oils dates back to 1930 when the I.G. FARBENINDUSTRIE A.G. proposed emulsion polymerization using benzoyl peroxide as a catalyst.

World War II gave great impetus to the copolymerization of styrene with oils. During the war, production facilities for styrene were tremendously increased because of the demand for synthetic rubber, and there has been a continuous increase since that time. The result has been a drop in cost of the monomer from 50 or 60 cents in 1935 to 21 cents in 1954. The favourable economic development together with the good qualities styrene imparts to copolymers such as light colour, inertness to alkali, good resistance to weathering, and non-yellowing characteristics have encouraged its use. Simple blends of polystyrene resins and oils have been investigated, but limited compatibility leads to poor quality in the resultant films.

Little work is recorded on styrene–oil copolymers in the period from 1931 to 1940. In 1940 STOESSER and GABEL (1940) described a styrene copolymer with less than 2 per cent of China wood oil. The product in this case was intended

to be slightly harder film former than China wood oil. A counterpart of this is described by Bass *et al.* (1940) in which oiticica oil was similarly treated. Light (1941) describes a series of reaction products of China wood oil, oiticica oil and styrene which were made by running the reaction for about 3 days between 80 and 140°C. These products had resinous and rubber-like characteristics.

The interim, 1940 to 1945, was again lean in published work on styrene copolymers. In 1945 Wakeford and Hewitt (1945, 1946) announced their important work on styrene copolymerization.

Basic processes. In the immediate post-war years, the two basic processes now used in styrene oil copolymerization were developed. They are the English or solvent process which was described by Hewitt and Armitage (1946), and the American, or Dow, or mass process described by Peterson (1948). In the first process, a blown or polymerized linseed oil, or a conjugated oil (China wood oil or dehydrated castor oil) (Rubens and Boyer, 1946) is treated with styrene with xylene as a cosolvent. In the second process the reactants, without solvent, are treated with peroxides or blown oils as a catalyst. These can be added at the start of the reaction or in increments as the reaction proceeds.

The emulsion polymerization method which was first described in 1931, and is widely used in the rubber industry today, does not find favour in oil–styrene reactions. Variations in styrene–oil copolymerizations, however, have been patented (Griess and Teot, 1949, 1953; Haines, 1952; Hewitt and Armitage, 1952; Robinson, 1951; Sleightholme and Hammond, 1952; Young and Hoogsten, 1949).

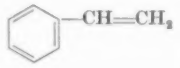
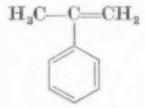
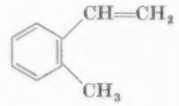
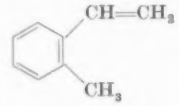
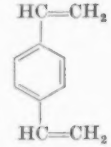
The styrene-type compounds used today are shown in Table 17. These include styrene (I); α-methyl styrene (II); vinyl toluene, a mixture of *meta-* and *para-*methyl styrene, (III); mono-methyl styrene, a mixture of *ortho-* and *para-*methyl styrene, (IV); and divinyl benzene (V). In the literature these compounds are referred to under various names, as vinyl aromatics or vinyl benzenes.

The methods used to prepare oil–styrene polymers must be adjusted to compensate for the faster rate of polymerization of styrene. In the early work this rate difference caused some difficulty in making truly compatible systems. With the availability of α-methyl styrene, divinyl benzene, and vinyl toluene for use in conjunction with styrene, the polymerization rates could be advantageously adjusted.

With these facts in mind Hovey and Jerabek (1951) have enumerated the advantages of the British and American processes from the technical point of view. Provided that explosion-proof equipment is available, the solvent (British) method has the advantages of: easier temperature control, reduction of the tendency of styrene to polymerize with itself, easier physical handling because of lower viscosities, especially if filtering is necessary, and an inert atmosphere (furnished by solvent vapours). The mass (American) process has the advantages of: full utilization of kettle capacity and high production output with limited equipment.

With the mass polymerization processes it is sometimes difficult to obtain

Table 17. Properties of vinyl aromatics

	I	*II*	*III*	*IV*	*V*
Synonym	*Styrene vinylbenzene*	*α-methyl styrene**	*Vinyl toluene m- and p-methylstyrene*[a]*	*Monomethyl styrene†[b]*	*Divinyl benzene*[c]*
Structural formula					
Molecular weight	104	118	118	118	130
Specific gravity 25/25°C	0·9045	0·9062	0·890		0·9182
Refractive index at 35°C	1·54389	1·53586	1·5342	1·5419	1·5605
Boiling point (°C) at 760 mm	145·2	165	170–171	172	195
Flash point (°C)	31	58	60	57	74
Freezing point (°C)	−30·6	−23·21	−82·5	−40	−87
Viscosity at 25°C (cps)	0·730		0·770		1·002

* Dow Chemical Co.
† American Cyanamide Co.
[a] Approx. 99% mixed isomers *m* and *p* methyl styrene.
[b] Isomers. *O*–33%, *m*–2%, *p*–65%.
[c] Approx. 45% in ethyl vinyl-benzene.

a truly compatible, homogeneous, clear copolymer, but by careful manipulation of the operating conditions such difficulties can be overcome. Hovey and Jerabek point out that thermal polymerization gives clear products only when the oil contains appreciable conjugation or when non-conjugated oils are employed with acidic catalysts. Examples of the latter are boron trifluoride and stannic chloride. It is known that these catalysts also cause oils to body, and no doubt this is their effect in the copolymerization reaction.

Hovey and Jerabek mention that peroxide catalysed styrenation of a non-conjugated oil gives a cloudy or hazy product, probably because of poor solvent tolerance. This is true using benzoyl peroxide or blown oils, or in blowing during processing.

Film and solution clarity has always been a problem with styrene copolymers. The addition of α-methyl styrene to the copolymerization reaction yields a satisfactory and clear product. This may be caused in part by the different polymerization rates of styrene and α-methyl styrene as compared with the oil used. The α-methyl styrene polymerizes at a much slower rate than styrene making its handling in the presence of oils easier.

Two classes of catalysts which are used to effect the styrene–oil copolymerization reaction have been mentioned, namely, peroxides and halides of metals and non-metals. Each class, according to Hovey and Jerabek, has its advantages and disadvantages. Advantages for the peroxide process are practical reaction speed, fairly good initial colour, a good working viscosity in thinner, extremely rapid air dry, better flexibility than the boron trifluoride type oils of equivalent composition, and good package stability. The disadvantages of the peroxide process are some degree of thermoplasticity and poor solvent resistance, lower film hardness and poor mar resistance, poor non-yellowing properties, poor compatibility with other film forming materials, poor tolerance for mineral spirits, and relatively poor heat convertibility.

The advantages of the non-metal halide process are excellent initial colour, good solubility in mineral spirits, short air-drying time, non-yellowing characteristics equivalent to comparable alkyds, interior gloss retention better than alkyds, good exterior durability at low levels, and low acidity, meaning low reactivity with active pigments and driers. Disadvantages of the non-metal halide process are very poor viscosity retention and reduction with mineral spirits, reaction rates at low styrene levels too slow to be practical, dry films are somewhat thermoplastic having poor mar and solvent resistance and some brittleness, incompatibility with other film formers, and poor heat convertibility.

From the large amount of work recorded in the literature to date, Hovey (1950) and Hovey and Jerabek (1951) have summarized the principles involved in the preparation of the styrene–oil copolymers. These principles are directed toward keeping the self-polymerization of the styrene as low as possible. They are as follows:

(a) The ratio of styrene to oil must be kept as low as possible during the course of the reaction; this can be achieved by a stepwise addition of styrene.

(b) If polymerization is carried out in the presence of a non-reactive solvent,

the limitation of the styrene to oil ratio is not as important. The presence of solvent helps to retard self-polymerization of the styrene. This characteristic applies when the oil is conjugated.

(c) The presence of conjugation in the oil favours copolymerization resulting in better homogeneity and mineral spirits solubility.

(d) Certain modifiers such as α-methyl styrene and terpenes are especially helpful in retarding styrene polymerization when the oils are low in conjugated unsaturation.

(e) In addition to heat, catalysts are necessary to promote the styrene reaction especially with oils low in conjugated unsaturation. The reaction can be promoted by active peroxides, by blown oil, or by blowing during the reaction to produce peroxides in the oil, and by halides such as boron trifluoride, stannic chloride, etc.

Some of these principles are illustrated in the early work of HANSEN *et al.* (1949). In order to study the effect of styrene concentration, he prepared a series of linseed copolymers containing 20, 30, 40, 50 and 60 per cent styrene, by a procedure using boron trifluoride.*

Table 18. *Copolymerization of linseed oil with styrene using* 0·4% *of boron trifluoride as a catalyst at* 93°C*

Product No.	*% composition*		*Reaction time* (min)	*Properties*				
	Styrene	*Linseed oil*		*Viscosities*†			*Colour at* 70% *N.V.*	*Sanderson*‡ *dry*
				100%	70%	50%		
B·2	20	80	15,540	134	2·59	0·84	10	5 : 30
B·3	30	70	3,960	1,092	5·9	0·98	12·7	20 : —
B·4	40	60	2,580	4,580	7·0	0·65	10·5	5 : 20
B·5	50	50	1,080	88,200	9·9	0·5	9·5	4 : 20
B·6	60	40	30	48,200	4·8	0·4	2·2	1 : 08

* According to HANSEN (1949).
† In mineral spirits as stokes.
‡ Using 0·2% Pb, 0·025% Co.

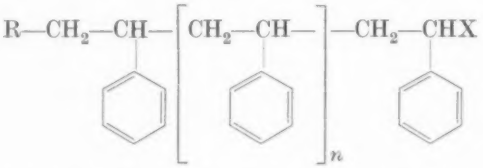
Table 18 indicates properties of boron-trifluoride-catalysed linseed–styrene polymers. These data show that the properties of the products vary markedly with styrene content. The 20 per cent styrene copolymer (B–2) reached a low

* A total charge of 600 g was used in a reactor equipped with thermometer and mechanical agitation. The catalyst, 0·4 per cent of boron trifluoride based on the styrene, was added to the oil stepwise over a period of 5 min at a constant temperature of about 65°C. When addition was complete the temperature was raised to 93°C, either by exothermic or external heat and maintained at this temperature until the control viscosity measurements showed the reaction to be finished. The mixture was then treated with 200 g of mineral spirits and steam-distilled. At approximately 177°C the colour bleached, indicating the removal of the catalyst. The steam was shut off and distillation under vacuum was continued until a temperature of 305°C was reached, to remove catalyst, mineral spirits and unreacted styrene. Weight loss at this point was negligible, indicating that the reaction was actually complete.

viscosity of 134 stokes at 100 per cent non-volatile after 11 days reaction time, whereas a 60 per cent copolymer (B–6) attained an extremely high viscosity of 48,200 stokes in only 30 min reaction time. The colour reached a maximum and the rate of film set-up reached a minimum at 30 per cent styrene and then both improved as the styrene level was increased. The greatest change occurred between 50 and 60 per cent modification. No explanation can be offered for the inferior colour and the very slow rate of film set-up at 30 per cent styrene level (B–3) as compared with the 20 and 40 per cent products (viz: B–2 and B–4). Repeat runs verified these observations.

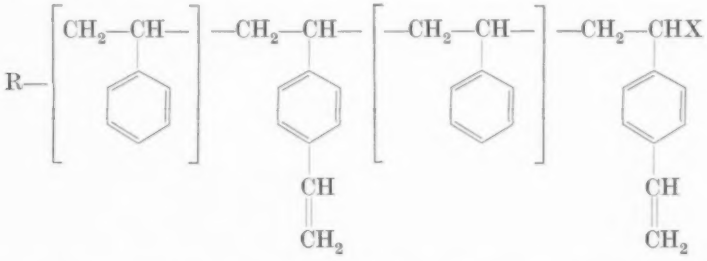
The viscosity retention of copolymer oils of Table 18 was very poor when thinned with mineral spirits. This can be ascribed to the type of polymer formed, one in which there apparently is very little cross-linking. The introduction of difunctional divinyl benzene into the styrene–oil system leads to the formation of cross-linked polymers with much better viscosity retention characteristics.

For non-cross-linked polymer, the following structure is postulated:



X is a termination group, and R is the unsaturated oil residue.

For the primary polymer chain using divinyl benzene the structure is considered to be:



The primary polymer chain for the styrene–divinyl benzene system as indicated above still contains vinyl groups which can react further to give a three dimensional structure.

Further work by Hansen utilizing the cross-linking effects of divinyl benzene is shown in Table 19. In this instance, linseed oil was copolymerized with a mixture of styrene and divinyl benzene with boron trifluoride as the catalyst. An inspection of these data indicates the beneficial effect on viscosity retention characteristics imparted to the system by divinyl benzene. The effect of divinyl benzene is illustrated by comparing product S–5 of Table 19 with product B–6 of Table 18. In the former, 1·25 per cent of divinyl benzene out of

Table 19. *Copolymerization of linseed oil with mixtures of styrene and divinyl benzene using boron trifluoride as a catalyst**

Product No.	*% Composition*		*Properties*				
	Total† styrenes	*Divinyl benzene*	*Viscosities (stokes)*			*Colour G-H*	*Sanderson‡ dry*
			100%	70%	50%		
S–1	30	4	64·3	—	—	4	2 : 45
S–2	35	4·8	61	—	—	4	2 : 20
S–3	38	6·8	4,600	—	2·2	4	1 : 30
S–4	43	6·8	7,550	—	4·6	1	
S–5	59	1·25	4,320	3·6	1·7	3	1 : 45

* According to HANSEN (1949).
† Total styrenes include the *o*-, *m*- and *p*-ethyl present in divinyl benzene.
‡ With 0·2% Pb and 0·025% Co driers.

a total monomer modification of 60 per cent gave the product a viscosity of 4,320 stokes at 100 per cent non-volatile as compared with 48,200 stokes for product B–6 having a 60 per cent styrene content. At 70 per cent non-volatile the viscosities were somewhat comparable i.e. 4·8 vs, 3·6 stokes. However, at 50 per cent non-volatile the product containing divinyl benzene had a much higher viscosity, i.e. 1·7 vs. 0·4 stokes.

As a class, the vinyl–benzene modified copolymers showed improved air-dry times and formed films with less thermoplasticity than those modified only with styrene. In varnish cooking procedures the copolymers containing divinyl benzene showed bodying rates approximating that of China wood oil.

Table 20 compares the properties of a 50 per cent linseed, 50 per cent styrene copolymer made by using two different catalysts, boron trifluoride and benzoyl peroxide. The boron trifluoride catalysed product set to a clear film and also gave clear solution when diluted to 50 per cent non-volatile with mineral

Table 20. *Comparison of the properties of* 50% *linseed–*50% *styrene copolymers using benzoyl peroxide and boron trifluoride**

Catalyst	*Viscosity (stokes)*	*Colour*	*A.V.*	*S.V.*	*I.V.*	*% Unsap.*	*Sanderson† dry*
BF_3 0·2%	1112	5	1·62	71·4	92·3	3·85	1 : 45
BzO_2 2·0%	429	4–5	2·99	69·2	91·5	19·10	3 : 20

* According to HANSEN (1949).
† With 0·2% Pb, 0·025% Co.

spirits. The benzoyl peroxide catalysed product gave a slightly hazy film and hazy solution in mineral spirits. The unsaponifiable content of the boron trifluoride catalysed product was 3·85 per cent as compared with 19·1 per cent

for the peroxide catalysed copolymer. Based on the latter data taking into account differences in the molecular weight of the soaps, it appears that there is a greater amount of polystyrene in the peroxide catalysed copolymer which explains the hazy solution and hazy film characteristics. In this connection KAPPELMEIER (1951) states that in most instances at least 12 per cent of the fatty acids are combined with the styrene in a 50 per cent modified product.

In order to compare the British process of Hewitt and Armitage and the American or Dow process, Hansen prepared a series of copolymers with conjugated and non-conjugated oils, modified with styrene and α-methyl styrene. The physical characteristics and composition of these products are described in Table 21. The polymerizations using the English process were carried out in refluxing xylene, and the polymerizations using the Dow process with blown oils were carried out in the absence of solvent. The reaction was checked for viscosity at frequent intervals in a petroleum solvent with a KB value of 80. A 70 : 30 ratio of styrene to α-methyl styrene was used for all blown-oil copolymerizations except the China wood–soybean combination which gave a hazy product at this ratio. In this case a ratio change of 60 : 40 gave clarity of solution.

In addition to the data of Table 21, analysis showed that in the British process, 80·5 per cent of the styrene reacted with dehydrated castor oil and 85·5 per cent reacted in the 35/65 China wood–soybean inter-ester. In contrast, the polymers made by the American process with blown oil contained between 90 and 95 per cent of the charged styrene.

In this comparative study it was observed that the American process using blown oils seems to be more versatile, since both linseed and soybean oils give practical products. The thermal polymerization in solvent is definitely limited to oils having some conjugation. The blown conjugated oils when styrenated definitely give more homogeneous products than the blown styrenated non-conjugated oils. The former are clear at 100 per cent non-volatile, and the latter, in the case of soybean oil, are not clear at 70 per cent non-volatile, even in a high-solvency solvent with a KB value of 80. The styrenated blown oil product made from the inter-esterified 35 per cent China wood oil, 65 per cent soybean oil combination is soluble in weak solvents indicating the marked effect of conjugation on the homogeneity of the product.

The products prepared by the American and British methods were subjected to weathering and durability tests, using standard varnish testing procedures. Results of the weatherometer tests are shown in Table 22. Products made by both processes showed excellent weatherometer durabilities in contrast to long oil alkyds which failed in about one-third of the time under similar conditions. The water-resistance and alkali-resistance of all films were excellent in relation to a 12½ gal varnish. All films showed good flexibility over a ⅛ in. mandrel at the end of 6 months, but the adhesion was only fair.

It has been previously mentioned that blown oils and oils containing conjugated unsaturation do not require activation with a catalyst. For the most part copolymers produced with these base oils are generally clear and homogeneous.

Table 21. Comparative results of the British and American processes for the styrenation of oils

Product No.	Base oil			Reaction charge (%)				Reaction conditions			Properties of products				
	Type	Visc. (stokes)	Peroxide value	Oil	Styrene	Methyl styrene	Xylene	Process	Time	Temp. (°C)	N.V.†	A.V.	Visc. G–H	Colour	Clarity
1	Linseed	1·00	0	25	25	—	50	British		143					Hazy
2	Linseed	30·00	70	50	35	15	—	American	4:30	171	50	0·88	F-G	8	Clear
3	Soybean	1·00	—	25	25	—	50	British		143					Hazy
4	Soybean	30.00	90	50	35	15	—	American	2:30	171	50	1·1	G	7	Clear
5	Dehydrated castor	0·14	—	25	25	—	50	British	64	145	45·1	1·05	I	5	Clear
6	Dehydrated castor	0·30	40·2	50	35	15	—	American	14	171	50·0	3·86	E	11–12	—
7	China wood soy	2·00	—	25	25	—	50	British	90	143	46·4	1·05	H	7–8	—
8	China wood soy	21·00	50·4	50	30	20	—	American	3:30	171	50·0	0·26	L	7–8	Hazy

* According to HANSEN (1949).

† All blown oil reactions were thinned to 50% of non-volatile content in Mineral Spirits (KB value = 80)

*Table 22. Performance data on products of Table 21 prepared by the British and American styrenation methods**

Product No.	Oil	Process	Sanderson dry (a)	Sward hardness					Cold water (b)		Boil water (c)		3% NaOH solution			Kauri reduction		Weatherometer exposure 60° Gloss readings at given time (h)							
				24 h tack	24 h	72 h	1 wh	2 wh	Bl.	Rec.	Bl.	Rec.	Bl.	Wr.	Fail	Pass	Fail	0	105	304	512	554	600	712	810
2	Linseed	American	0 : 30	Tack-free	24	26	28	30	L	1 m	M	5 m	—	2 h	22 h	50	60	100	76	73	60	—	40	14	Fail
4	Soybean	American	0 : 45	Tack-free	15	16	20	22	VL	1 m	H	2 m	—	40 m	16 h	70	80	102	75	45	50	—	32	Fail	
5	Dehydrated castor	British	0 : 10	Tack-free	20	22	26	26	L	1 m	H	1 m	13 m	23 m	10 d	70	80	95	78	70	67	—	46	25	Fail
6	Dehydrated castor	American	0 : 30	Tack-free	22	28	30	32	VL	1 m	H	1 m	5 m	13 m	16 d	50	60	103	77	80	62	35	Fail		
7	China wood soy	British	0 : 12	Tack-free	16	20	26	26	H	10 m	H	60 m	5 m	13 m	48 h	60	70	86	75	70	55	58	Fail		
8	China wood soy	American	0 : 50	Tack-free	15	15	16	16	VL	1 m	H	3 m	2 m	8 m	2 h	60	70	100	75	52	57	—	45	20	Fail

* According to HANSEN (1949).
(a) 0·2% Pb and 0·025% Co as % of metal on a non-volatile basis were added as naphthenates.
(b) One inch wide tin strips were dipped into vehicle containing driers and after 48 h of drying at 77° F and 50% relative humidity the strips were immersed in distilled water for 48 h. The degree of blushing (Bl.) was recorded as very light (VL), light (L), medium (M), or heavy (H). The number of minutes (m), hours (h), or days (d) to recover (Rec.) was recorded as a measure of water-resistance.
(c) Panels prepared were immersed in boiling water for 15 min. The degree of blushing and rates of recovery measure the relative resistance boiling water.
(d) Test tubes were dipped into the vehicle with driers and after 72 h of drying were immersed in 8% alkali. Blushing, wrinkling (Wr.) and failure were observed.

This observation appears to be subject to certain limitations. Many blown linseed and soybean oils (HOVEY, 1950) will styrenate to clear homogeneous products, while unblown base oils will not. The question is to what extent the oils should be blown. YOUNG (1949) points out that a minimum peroxide value of about 360 for a blown soybean oil will yield a homogeneous copolymer. HOOGSTEEN and YOUNG (1950) conclude from their work on the styrenation of dehydrated castor oil, by either mass or solvent methods, that the most desirable products are obtained when the castor oil is dehydrated as far as possible and then bodied to about 15 stokes. Although a Dow Patent (1951) covers oils with less than 35 per cent of conjugated unsaturation, it appears that minimum conjugation in an oil should be 25 per cent of the unsaturation to obtain the most desirable copolymers.

There are several patents relating specifically to the use of the reaction products of blown oil and vinyl aromatic hydrocarbons. SAMPLE (1953) described a method of making a vinyl aromatic–blown oil copolymer which dries to a gasoline resistant film. A linoleum binder is described by DUNLAP (1945) in which a copolymer is made of blown oil, styrene and another vinyl compound. NYE (1951) describes a similar reaction in the presence of heptane as a solvent, from which the styrene–oil copolymer is precipitated with methanol. BRUNNER (1953) prepared a copolymer from a blown oil and up to 10 per cent of a vinyl aromatic hydrocarbon, for use in thinning alkyd resins.

Other reaction modifiers. The styrene–oil copolymerization reaction is also catalysed by sulphur dioxide (ARVIN, 1953; BERGER & SONS, 1952) or by a combination of anthraquinone with sulphur dioxide (ANON., 1952b). Transfer agents such as carbon tetrachloride, symmetrical dichloroethane, di- and triphenyl methane, tetrabromo ethylene, fluorene, ace-naphthene and pentaphenyl ethylene have been used to minimize cross-linking in styrenation reactions according to BRADSHAW and EVANS (1952). ARMITAGE (1954) has recently shown that active earths, e.g. Fuller's earth, hydrosilicates, bentonites, etc. will act as catalysts for the copolymerizing of vinyl aromatics and conjugated oils.

In order to control the polymerization reaction, the use of chain terminators is suggested. Wakeford *et al.* 1946 mentioned the use of a terpene for this purpose. The importance of terpenes as chain terminators is reflected by the number of patents which have been issued (ARMITAGE, 1953; ARMITAGE and SLEIGHTHOLME, 1952; WAKEFORD and HEWITT, 1951, 1952).

A series of patents also describe the use of sulphur as a chain terminator (HAMMOND, 1951; SLEIGHTHOLME and HAMMOND, 1952; WAKEFORD and HAMMOND, 1950; WAKEFORD, SLEIGHTHOLME and HAMMOND, 1950) for both oil and alkyd resin styrenations. The combined effect of sulphur and terpenes is also disclosed (SLEIGHTHOLME and HAMMOND, 1952).

B. Styrene–fatty acid copolymers

The styrenation of fatty acids is recent. BHOW and PAYNE (1950) treated conjugated fatty acids with styrene by the mass process using benzoyl peroxide

as catalyst. They found good agreement between the observed increase in weight and the change in acid value. The reaction products appear to be true copolymers. POWERS (1950) showed that styrene will react with oleic acid at 160°C and with linseed acids between 160° and 275°C to form polymers which contain between 1 and 25 styrene units. Higher temperatures produced more soluble products. There is no evidence indicating the presence of uncombined polystyrenes. This observation is in agreement with that reported by DYER and MAXWELL (1949) in which ethyl linoleate was copolymerized with styrene to form a product containing about 13 styrene units.

Styrenated fatty acids can be treated further with polyols such as glycerol or pentaerythritol according to BHOW and PAYNE (1950) and KANNING and HART (1953) to produce styrenated oils. BOBALEK (1951) described a related process in which the polystyrenated acids are reacted with phenolic resins and then esterified using litharge or calcium stearate as catalysts.

C. Styrene copolymers with modified oils

Maleic modified oils have been prepared and reacted with styrene. A product of this type is described by RUST (1946) in which a diglyceride is treated with maleic anhydride at a low temperature and then copolymerized with styrene using benzoyl peroxide catalyst. WEISGERBER and DYER (1954) describe a similar product in which the esterification product of linseed acids and butandiol-1, 4 was reacted with styrene below 80°C with benzoyl peroxide as the catalyst. Related to these products, KIRK (1948) describes a coating for metal in which the reaction product of stearyl alcohol and maleic anhydride (distearyl maleate) is copolymerized with styrene. DYER and MEISENHELDER (1951) disclose the preparation of styrene copolymers with esters of the type 2-chloro allyl linoleate using benzoyl peroxide or stannic chloride as catalysts. They indicate that the product containing a high proportion of ester is infusible.

D. Vinyl–toluene copolymers*

Certain shortcomings of styrene as a copolymer material with oils were recognized by the DOW CHEMICAL CO. and therefore they introduced vinyl toluene (1953) which in a measure overcomes some deficiencies of styrene. This material is easier to handle than styrene. The following advantages for vinyl toluene are cited by HENSON (1953): It forms copolymers which are compatible with modifiers over a wider composition range, can be used with either tall or fish oils with equal facility and is easier to react than styrene, thus reducing kettle time. The polymers possess infinite tolerance for low KB thinners. On a pound for pound replacement economic considerations favour vinyl toluene.

BUEGE (1954) prepared a series of vinyl toluene–linseed copolymers and concludes the following: Film clarity of the copolymer of an unconjugated oil is a direct function of the iodine number of the oil. With conjugated oils uncatalized reactions yield clear products. With 4·35 stokes viscosity linseed

* Vinyl toluene is the terminology introduced by the Dow Chemical Co. (cf. Table 17).

oil the product clarity improves with catalyst concentration, or by use of slowly decomposing catalysts. Product clarity improves with increasing polymerization temperatures. Product viscosity increases with catalyst concentration in the case of di-*tert*-butyl peroxide and 2,2-bis(ter-butyl-peroxy) butane catalysed products.

E. Styrene copolymers with esters of tall oil

Vinyl tall oil esters* have been investigated as a copolymer component. Marling (1952a) disclosed a solvent method for preparing a polymerized vinyl tall oil using anthraquinone as a catalyst. This product was reacted with a combination of styrene and dehydrated castor oil to form a vehicle. Vinyl tall oil esters have been treated with styrene and *iso*propyl biphenyl, *iso*propyl benzene, vinyl biphenyl or *iso*propenyl biphenyl (Marling, 1951) at reflux temperatures. The products are complex styrene copolymers. Tall oil esters of polyhydric alcohols and polybasic acids have also been copolymerized with styrene according to Schmutzler (1952).

F. Nature of the styrene–oil reaction

A number of investigators have attempted to establish whether styrene and oil actually copolymerize, or whether both polymerize individually to mutually soluble polymers. Visual observations of the clarity of styrene–oil copolymers, in dry films and in solution have led most investigators to believe that the reaction is one of true copolymerization.

Terrill (1953a) states that 'the conflicting results and theories presented in connection with the styrenation of drying oils are in large measure due to the wide range of conditions and reactants employed.'

Falkenburg *et al.* (1951, 1952) carried out a detailed investigation of the styrenation of methyl esters of various fatty acids. The products were studied for film clarity and the possibility of separation of polymers. They conclude that 'data show no copolymerization between the fatty esters and styrene occurs and that homogeneity of some of the reaction products cannot be considered as proof for inter-polymerization.'

Harrison and Tolberg (1953) on the other hand, point out that styrene does copolymerize with compounds containing conjugated unsaturation but the amount of copolymerization is small.

It appears that considerable work remains to be done to establish the composition and structure of the oil–styrene or methyl–styrene copolymerization reaction products.

At this point several comments concerning the reaction mechanism should be made. First it has been previously stated that either blown oils or conjugated oils will react readily with styrene to produce clear and homogeneous systems. In the case of blown oils it was indicated that peroxides formed during blowing catalysed the reaction. In non-conjugated systems it was also indicated that peroxides or halides were necessary to promote the reaction. Secondly, it is

* These esters are made by the processes described under the section on vinyl esters (p. 242).

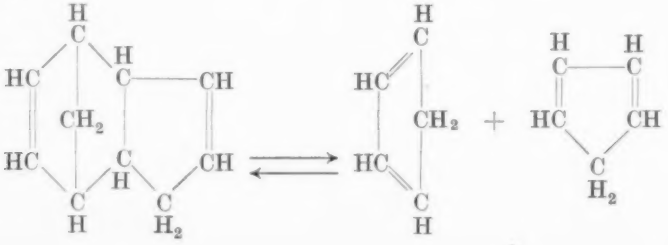
recognized that allylic hydrogens are reactive under certain circumstances. This may be particularly true of allylic hydrogens in conjugated systems under the conditions employed in copolymerization. RINSE and KORF (1949) believe that the reaction between styrene and oils occurs at an α-methylene group relative to a double bond. The activity is influenced by metals and acids and is very sensitive to temperature changes. Thirdly, it has also been pointed out that oils with some degree of polymerization react more readily than unbodied oils. It is known that during the oil-bodying process there is a shift from non-conjugated to conjugated structures, which are capable of reacting with styrene. Finally, in the previous discussion it was mentioned that sulphur dioxide and anthraquinone have been used in copolymerization reactions. These compounds were previously described as conjugation catalysts. It appears that under the influence of these compounds conjugation can be induced simultaneously with the oil–styrene reaction. All of the processes, whether chemical, thermal, or catalytic, serve either to enhance the reactivity of a carbon atom α to a double bond or to form reactive conjugated systems. Therefore, circumstantial evidence points to the possibility that the styrene could attach itself to this carbon atom, as well as to react directly with the conjugated groups.

G. cyclo*Pentadiene and di*cyclo*pentadiene copolymers*

*cyclo*Pentadiene and its dimer, di*cyclo*pentadiene, are available in commercial quantities as a by-product from petroleum and coal-tar processors. Based on their low cost, availability in large volumes, and chemical reactivity they have been attractive as raw materials for modifying drying oils.

An extensive review of these olefins by WILSON and WELLS in 1943 does not mention their use with drying oils. The earliest published reports date from GERHART in 1944, who claimed methods for treating *cyclo*pentadiene with oils in the presence of a catalyst such as boron trifluoride or the halides of amphoteric metals. Upon completion of the reaction, the catalyst can be neutralized with a base. Products containing up to 40 per cent of *cyclo*pentadiene are described. Similar products can be prepared without the use of a catalyst according to ADAMS and GERHART (1945).

It does not seem to be too important whether the monomer or dimer of the *cyclo*pentadiene is used in the oil copolymerization reactions. Under the influence of heat, which is necessary to effect the reaction, the di*cyclo*pentadiene will dissociate into two molecules of monomer according to the following equation:



The quality and degree of polymerization of *cyclo*pentadiene is immaterial. It would appear that the polymers gradually dissociate to give monomer which is used up in the oil reaction, thus favouring further decomposition. The early grades of di*cyclo*pentadiene contained about 65 per cent of the diolefin. The quality has been improved so that there is now 96 per cent of diolefin available in current commercial products.

The copolymerization reaction can be carried out at temperatures in the range of 200°–315°C. In some instances, closed systems are used and in others the reaction is conducted at atmospheric pressures.

A series of *cyclo*pentadiene-modified oils was prepared by HANSEN *et al.* (1945) using 65 per cent di*cyclo*pentadiene.* Some typical data from Hansen's work on the preparation of 'di*cyclo*' oils are shown in Table 23. The copolymers described in this table, when compared to the styrene copolymers of Tables 18, 19 and 21 showed better film forming characteristics. They exhibited fast hard dry, good flexibility, and excellent compatibility with modifying agents. Film adhesion was good. Their set-up time seems to be a function of the degree of polymerization, measured by viscosity, as shown by products designated as D-3, D-4 and D-5 of Table 23. Products which have about 20 per cent of combined *cyclo*pentadiene are good varnish oils, and have been used as a replacement for China wood oil.

MUNDY and MALYAN in 1953, disclosed methods for preparing *cyclo*pentadiene copolymer oils in which the olefin is varied up to 400 parts per 100 parts of refined or unrefined oils. The reaction is run without catalysts, or with a peroxide such as benzoyl peroxide.

Maleic anhydride modified oils have also been reacted with di*cyclo*pentadiene. WYNSTRA (1952) discloses the preparation of maleic-treated oils copolymerized with di*cyclo*pentadiene. GERHART and ADAMS (1948) also describe a method for preparing soybean maleic copolymers of di*cyclo*pentadiene.

GERHART (1946) has also disclosed mixed products made by treating oils with ester gum or other hard resins, followed by copolymerization with *cyclo*pentadiene. In 1953 he also used a terpene, such as limonene or camphene, in the copolymerization reaction. An insoluble vulcanizate can also be prepared according to GERHART (1949) by reacting a *cyclo*pentadiene oil copolymer with sulphur.

Tall oil has been reacted with *cyclo*pentadiene according to PETERS (1952) using pressure and no catalyst. The copolymerized acids are subsequently reacted with polyols to form varnishes.

The *cyclo*pentadiene oils prepared with or without catalysts are relatively poor grinding vehicles. MOFFETT and HOYA (1951) disclosed a method for improving the pigment wetting characteristics of oils of this type. The

* The *cyclo*pentadiene was charged with the oil into a mechanically agitated and heated autoclave. The system was sealed and heated to temperatures from 205–310°C with a resultant pressure of 33 to 100 p.s.i. As the reaction proceeded the pressure dropped to a range of 15 to 20 p.s.i. The course of the copolymerization reaction was studied by checking viscosity at intervals. At the conclusion of the reaction, the unreacted hydrocarbons were removed by distillation or steaming. The amount of copolymerization which took place during the reaction was determined on a weight balance basis.

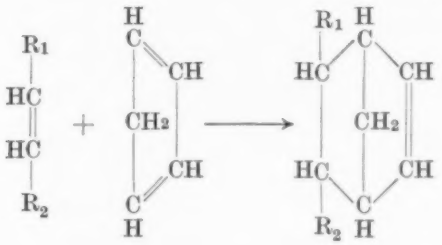
*Table 23. Constants and properties of linseed dicyclopentadiene copolymers**

Product no.	*Reaction conditions*		*Combined dicyclo (%)*	*Constants of products*				*Sanderson dry* (h)	*Performance of products*				
	Temp (°C)	*Time* (h)		*Colour*	*% N.V.*	*V, stokes*	*%Unsap.*		24 h	72 h	1 wk	2 wk	*Kauri red*
D–1	287·8	4:00	7·5	8–9	100	44·3	—	2					
D–2	287·8	7:00	13·6	9·2	100	103	—	1:20					
D–3	290	1:48	19·2	9+	99·6	47·5	4·53	2:40				16	
D–4	285	4:30	20·0	12+	100 50	2900 2·0		1:15					
D–5	287·8	3:30	20·1	9	100 70 50	622 5·8 1·0		1:30	12	18	28		90–100
D–6	287·8	2:00	33.9	6	70 100	9·7 3600		0:50	24	36	52	52	20–30
D–7	268	2:30	38·5	10	50	0·7		1:0					0–10
D–8	282	:45	48	14	50	1·8	3·41	0:50	62	60	62	66	0
D–9	287·8	1:30	60	gelled									

* According to HANSEN (1949).

improvement is achieved by copolymerizing a half fatty acid ester of a 'cellosolve' or 'carbitol' with the oil and *cyclo*pentadiene.

The published literature on *cyclo*pentadiene copolymer oils is not as voluminous as that pertaining to styrenated oils. Consequently controversial questions concerning the structure of *cyclo*pentadiene copolymers have not arisen. There is little recorded concerning the polymer structure. TERRILL (1953a) suggests the following reaction for a fatty acid chain and *cyclo*pentadiene,



Since 1945 large amounts of *cyclo*pentadiene copolymer oils have been used by the protective coating industry. These have served as vehicles *per se* or have been modified with resins. They have been widely accepted because of their good performance characteristics. Exact production figures for the volume of *cyclo*pentadiene and styrene oil copolymers are not available. In spite of the greater publicity given the latter, the *cyclo*pentadiene oils appear to outsell the styrenated oils.

H. Copolymers with aliphatic olefins

Olefins derived from petroleum sources and ranging in molecular size from ethylene up to compounds having molecular weights as high as 500 have been copolymerized with oils. These olefins have been used either as monomers or as polymers. Butadiene and isoprene were recognized in 1929 (I. G. FARBEN) as potential materials for making linseed oil copolymers using carbonyls of iron, nickel, cobalt, molybdenum, tungsten and chromium as catalysts. Other catalysts for the same reaction are aluminum chloride, boron fluoride (I. G. FARBEN, 1933; RUMMELSBURG, 1945), stannic chloride (RUMMELSBURG, 1945), phosphoric acid on Fuller's earth (RUMMELSBURG, 1945), and peroxides such as benzoyl peroxide (I. G. FARBEN, 1933) or peroxides present in blown oils. Copolymers of hexadiene, isoprene, etc. with China wood oil have also been described (DAYTON SYNTHETIC CHEMICALS, 1937; PETERS, 1952). Up to 1951, the literature concerning the copolymers of glyceride oils and the olefins considered in this section is scarce, and the major portion of the work appears to have been recorded since then. In 1945 ROSTLER and BORNSTEIN treated oils with 'Naftalan hydrocarbons', which are compounds coming from the furfural insoluble material of petroleum refining. The resulting products were used as resins in varnish cooking procedures. BLOCH (1945) described the reaction of olefins of 2–8 carbon atoms with linseed oils using either peroxides or anthraquinone catalysts. TRACY (1951) treated linseed oil with di-*iso*butylene and butadiene using

aluminium chloride catalyst. Sparks and Field (1943) describe the *iso*butylene copolymers of China wood and oiticica oil or their acids prepared by solution polymerization using boron fluoride as a catalyst. A modification of the above copolymer oils is described by Marhofer (1951) who treated a linseed oil with 'Clay tower polymers.' This product was further reacted with butadiene and isoprene. A similar composition used as linoleum cement is described by Elliot (1952).

Another group of patents concern copolymers prepared from oils and synthetic olefins of higher molecular weights. Products obtained from open chain conjugated diolefins and triolefins having between 4 and 10 carbon atoms are claimed by Hillyer and Edmunds (1952). Bloch and Hoffman (1950) copolymerized oils and polyolefins with molecular weights of 200–400 under pressure. Gieser 1953 used polyolefinic cyclic hydrocarbons having molecular weights of 250–450 containing 2–4 double bonds per molecule, 70 per cent of which were conjugated. Copolymerization was conducted in the temperature range of 300–450°C with boron fluoride. Verley (1952) disclosed oil copolymers prepared from trimers and tetramers of butadiene. Geiser 1951 has also described the use of polymer gasoline made from olefins, butylene and propylene in this reaction. The products are co-bodied with linseed oil to yield varnishes.

I. Copolymers with other unsaturates

Terpenes. Rummelsburg (1945a) reacted terpenes, such as pinene, camphene, allo-ocimine, fenchene and other isomers, with drying oils in the presence of phosphoric acid or Freidel–Crafts catalysts to yield vehicles for paints, enamels and varnishes.

Divinyl acetylene. There is no indication that acetylene has been polymerized with drying oils. However, divinyl acetylene has been reacted with China wood oil and other oils in the presence of a small amount of maleic anhydride according to Collins (1937).

Furan derivatives. Furyl ethylene (Mighton 1946) has been copolymerized with linseed oil above 175°C in the presence of potassium carbonate and benzoyl peroxide catalysts. It is stated that an oil of this type has better film-drying characteristics than an untreated linseed oil. A brake-lining product made by copolymerizing a mixture of a drying oil, furfural and mesityl oxide in the presence of sodium hydroxide is described by Harvey (1951).

Ralston *et al.* (1948) disclosed a process for making an oil adduct with fish oil and furfural or coumarone using Friedel-Crafts catalyst. The reaction is conducted in carbon tetrachloride or nitrobenzene.

'*Neoprene*': Huff and Clynch (1944) claim a thermal copolymer of chloroprene (Neoprene). The products are either varnishes or plasticizers, depending upon composition.

Acrylic compounds. Bruson and Niederhauser (1948a, b), Opp and Werner (1951) and Mighton (1944) have shown that monomeric acrylic esters can be reacted with a drying oil fatty acid having conjugated double bonds, or an ester of these acids. A polymerization inhibitor is required. China wood oil or

oiticica oil ester gum varnishes can also be reacted with acrylates or methacrylates according to FLINT and ROTHROCK (1942). Conjugated oils have been copolymerized with acrylonitrile (SCHMUTZLER, 1952).

Mixed copolymers. BLOCH and GEISER (1952) and CARLICK (1954) disclosed the reactions of styrenated oils with butadiene and peroxide catalysts. The simultaneous styrenation of reaction mixtures of crotonic acids with fatty acids and a drying oil are described by BOBALEK (1949). NELSON and GLEASON (1953) prepared mixed butadiene–styrene copolymers of oils and POWERS (1946) prepared rubbery products from oils, butadiene and styrene. Styrene polyallyl ethers are disclosed by ROACH (1954).

MARLING (1952b) claims that a phenol–styrene oxide reaction product is compatible with styrenated oils and alkyd resins, while phenol–formaldehyde resins are incompatible. EVANS *et al.* (1953) describe the reaction products of vinyl phenol and blown oils.

Polyallyl copolymers. Esters of polyallyl alcohol have been discussed in the section on 'Synthetic oils' (p. 187). Allyl copolymers which are related to these products, are obtained from the reaction of an oil and an allyl ester. Reaction products of this type were prepared by BRADLEY (1948) and KROPA (1948) who copolymerized diallyl fumarate, adipate, phthalate and succinate with oils and alkyd resins by heating. In addition, a Dutch patent (N. V. DE BATAAFSCHE PETROLEUM MATTSCHAPPIF, 1953) describes the reaction of diallyl esters of dimerized fatty acids and diallyl phthalate to give a product which can be used as a coating material after the addition of driers.

The use of a third ingredient in the copolymerization is also described. Products with improved film-forming characteristics are prepared by treating linseed oil, an allyl ester and a styrene according to POLLY (1952). WEBER (1949) claims compositions which are copolymers of allyl linoleate with styrene, butadiene and isoprene. These reactions yield rubber-like materials.

ZIEF (1949) describes allyl sucrose. It is an oily compound which will dry by itself. It is compatible with natural drying oils and is stated to be an upgrader for linseed and soybean oils. When added to drying oils, followed by blowing, the dry film of the product shows improved hardness, reduced drying time, and improved resistance to solvents. Best results are obtained with allyl sucrose containing 5 allyl groups per sucrose residue (ANON, 1952a). FISHER *et al.* (1952) describe other alkenyl ethers, e.g. methallyl derivatives of glycols, glycerol, sorbitol, dipentaerythritol and other polyols; like allyl sucrose they can be used to upgrade the drying properties of various oils.

VIII. Vinyl Copolymers and Esters

Vinyl resins have unique and desirable properties quite unlike those of drying oils. Since the end of World War II production facilities and uses of vinyl resins have shown a phenomenal growth. For many end uses, these resins have replaced drying oils and drying oil products. From a study of the properties of vinyl resins and drying oils, it became apparent that technologically important products should result if vinyl resin and drying oil properties could be combined.

Vinyl resin properties would upgrade oils and drying oil derivatives would impart plasticizing and improved adhesion characteristics to vinyls.

Research to achieve this end has followed several courses, involving development of the following materials: vinyl–oil copolymers, ether and acetal complexes, and simple and complex vinyl esters of drying oil fatty acids.

A. Vinyl-glyceride–oil copolymers

A disclosure in 1933 by I. G. FARBEN showed that unbodied linseed oil could be polymerized with vinyl acetate, vinyl chloride or other vinyl containing compounds. Similarly, a bodied linseed oil fraction obtained by alcohol segregation was copolymerized with vinyl acetate using benzoyl peroxide catalyst by EIBNER *et al.* (1933).

DU PONT chemists (1942b, 1943) pointed out that vinyl esters of monocarboxylic acids could be inter polymerized by heating with a frosting type of oil such as China wood oil or its ester gum varnishes. ROTHROCK and WAYNE (1949) prepared the copolymer of vinyl chloride and an oil in which an unsaturated haloethylene was used to effect a mutual combination of the two ingredients. These products are said to have outstanding adhesion to metals.

Other types of vinyl copolymers have been described. WOLFF (1942) showed that vinyl ethers could be polymerized with tall oil esters other than the vinyl esters. A typical example of this process (WOLFF, 1943) cites the preparation of a polymer starting with a tall oil glycerol ester, vinyl ethyl ether, and diethylene glycol divinyl ether.

B. Vinyl ethers and acetals

Various reactions of oils and products of polyvinyl acetals or butyrals have been described. PRATT (1947) described a product consisting of a mixture of alcoholized linseed oil and 25–75 per cent of a low viscosity polyvinyl butyral. GROFF (1950) and POWERS (1945) describe the reaction of polyvinyl butyral with rosin and fatty acids by heating at temperatures in the range of 270°C–280°C until the mixture becomes clear.

C. Vinyl esters of fatty acids

The preparation of polyvinyl C_{18} fatty acid esters has been a challenge to drying oil chemists. Polyvinyl alcohol is difficult to handle because of its high molecular weight and solubility characteristics. Consequently, methods to prepare its esters have been unusual. No early records were found to indicate that vinyl esters of drying oil acids were prepared. The vinyl ester of 'trioxystearic' acid the constitution of which was not explained, is described by HERMANN and HAEHNL (1927).

A number of methods have been described for preparation of vinyl derivatives.

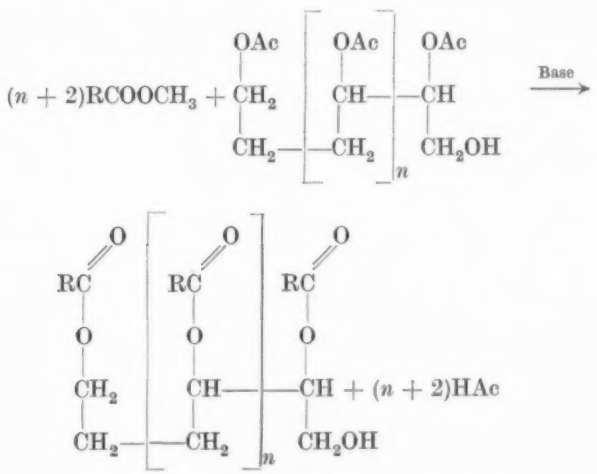
Monomeric vinyl esters by vinylation. REPPE (1936, 1940) treated fatty acids under pressure with acetylene diluted with nitrogen in the presence of a zinc salt or oxide as a catalyst:

$$HC{\equiv}CH + RCOOH \xrightarrow{Zn} RCOO{-}CH{=}CH_2$$

Zinc oxide (zinc soap) is preferred for fatty acids higher than six carbon atoms. HANFORD and FULLER (1948) describe a similar method in which potassium hydroxide is used as the catalyst. CHRIST and WUERTH (1949) prepared vinyl esters of short-chain acids in yields of 85–95 per cent. A modified direct vinylation process not requiring high pressures is described by RINSE and DORST (1948) and elsewhere (CARPENTER, 1946; REPPE, 1940). The fatty acids are placed in a vertical heated column, and acetylene diluted with nitrogen is passed through the mixture containing a zinc oxide catalyst. This type of reaction was used in Germany during the war for the preparation of vinyl tall oil esters which were used in lieu of the usual oils in protective finishes. The products prepared in this manner were identical to those prepared in the high pressure systems of Reppe.

Monomeric vinyl esters by acidolysis. In this method, monomer vinyl acetate is treated with a fatty acid in the presence of a freshly prepared mercuric sulphate catalyst (SWERN and JORDAN, 1950; TOUSSAINT and MCDOWELL, 1942). The vinyl ester is separated from the mercury catalyst and displaced acetic acid by distillation.

Preparation of polyvinyl esters by ester interchange. ECKEY (1951) described a process for ester interchange of a polyvinyl acetate and methyl esters of fatty acids. The process involves the following reaction:



This process requires a mutual inert solvent for the polyvinyl acetate and methyl esters in order to bring them into intimate contact. The catalyst is a basic compound such as sodium hydride or finely divided lithium, sodium or potassium. The preferred solvent is an ether, e.g. di-*n*-butyl ether, benzyl ether, dioxane or polyglycols. The interchange is complete in 30–60 min in the low temperature range of 50°–110°C.

Direct esterification methods. Polyvinyl alcohol is insoluble in fatty acids and direct esterification methods can not be used. RHEINECK (1951) and SCHERTZ

(1952) esterify polyvinyl alcohol with drying or semi-drying oil fatty acids without catalyst in the presence of a mutual solvent, phenol. The polyvinyl alcohol is dissolved in the phenol. Fatty acids are gradually added at a rate which maintains solution homogeneity while the phenol is simultaneously distilled. When the phenol has been removed, the product is freed of unreacted fatty acids by alcohol extraction.

Polymerization of monomeric esters. Polymers of monomeric vinyl esters, e.g. of linseed and soya acids, have been prepared (HARRISON and WHEELER, 1951) with difficulty using a peroxide catalyst. These products dry poorly in contrast to the excellent dry of the polyvinyl esters of Eckey and Rheineck. It appears that polymerization does not proceed solely through reaction of the vinyl group. Apparently the unsaturation in the fatty acid residues of the molecule also enters in the reaction, to give a non-oriented structure.

The polyvinyl esters made by the process of ECKEY (1951) and RHEINECK (1951) have a definitely oriented structure and there is no chance for a haphazard, non-oriented type polymerization since the ester is made from a pre-formed polyvinyl ester or alcohol. Such products exhibit unusual drying characteristics when treated with traces of cobalt driers. Films prepared from these esters dry tack-free in 20–30 min but are not hard. They show a somewhat 'cheesy' structure which is gradually eliminated upon ageing up to 24 h. After this time films become very tough and acquire some of the characteristics of vinyl plastics. Such films have unusual durability in outdoor exposure tests as mentioned by Rheineck.

Polyvinyl oleates prepared by either the Eckey or Rheineck processes will dry tack-free in several hours. Eckey demonstrated that even tallow esters dry. This is remarkable, since tallow is composed of about equal parts of saturated and oleic acids. Oleic esters prepared by polymerization of monomeric vinyl oleate with peroxide catalysts, followed by extraction to remove the non-polymer fraction, do not show the good drying characteristics possessed by the ester made by the direct esterification processes. This again shows that an oriented structure having the unsaturation in the fatty acids portions of the molecules free for oxidation reactions is necessary for good film formation and integrity.

None of the processes described above for the preparation of drying type polyvinyl esters have been successful on a commercial scale. The ester interchange process of Eckey is difficult to manipulate and yields as by-product a large volume of methyl acetate which would have to be recoverable and returned as a credit against the cost of the ester. The low yields, i.e. 50–60 per cent obtained in the direct esterification process using phenol, followed by the necessary phenol recovery, are economic disadvantages.

It was previously indicated that the polymerization product of monomeric vinyl esters was not satisfactory, especially in the case of vinyl linoleate. Vinyl tall oil esters seem to perform somewhat differently, probably because of the presence of rosin. These products were used in Germany for finishes during the war. Improved vinyl tall esters have been disclosed by MARLING (1952c).

He describes a process for polymerizing vinyl tall oil esters with an anthraquinone catalyst (MARLING, 1952a) and claims that the product exhibits improved drying characteristics. Copolymerization with styrene and *iso*propenyl biphenyls (MARLING, 1951) leads to further improvements.

Reaction of monomeric vinyl esters of saturated acids with other polymerizable compounds have also been reported. POWERS (1946) prepared copolymers with butadiene, and also tricopolymers with a third ingredient, e.g. styrene or acrylonitrile, using the emulsion method. The resulting latex was coagulated and compounded into an elastomer which was stated to have good tear-resistance. Other vinyl esters of fatty acids have been prepared in a number of cases. (BAUER *et al.*, 1952; NEHER *et al.*, 1952; PORT *et al.*, 1951, 1952a, b; SWERN and JORDAN, 1948, 1949).

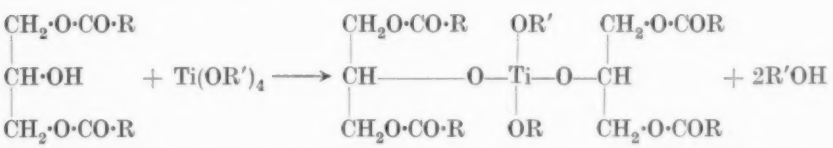
IX. Miscellaneous Methods For Improving Oil Properties

A. Cross-linking agents

Compounds which will react with two or more molecules of oil, and act a bridge between them are considered in this discussion as 'cross-linking' agents. Both organic and inorganic materials are used in this manner to give increased viscosity and harder dried films.

1. *Inorganic compounds*

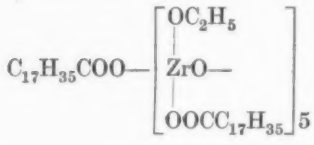
Early work on the use of titanium compounds as cross-linking agents dates back to NELLES (1935, 1936) according to information divulged in post-war reports of the German chemical industry. BOYD and GREEN (1952) showed that *ortho*-titanic and *meta*-titanic acids are gelation accelerators for oxidized or blown oils. KRAITZER *et al.* (1947, 1948), in Australia, showed that titanium alkoxides (alkyl *ortho*-titanates) could be used as cross-linking agents for mono- and di-glycerides and alkyd resins. A typical reaction utilizing two of the four available alkoxyl groups is as follows:



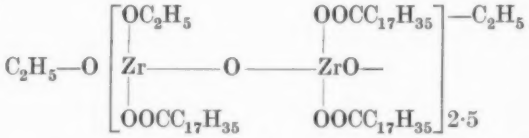
Other compounds containing free hydroxyl groups also react with titanium compounds according to the equation shown. The titanium acts as a bridge between two or more molecules. Carboxyl groups can also be treated. According to LANGKAMMERER (1952), compounds of the general formula, $(RO)_2Ti(OOCC_{17}H_{35})_2$, are formed if stearic acid is the reactant. With either hydroxyl or carboxyl groups, an alcohol is liberated. Titanium tetra-ethoxide, *iso*propoxide or butoxide are usually used.

A similar reaction has been described recently by BALTES (1954) in which zirconium alkoxides are used. In this instance, zirconium compounds of the

general type $Zr(OR)_4$ are treated with either linseed or stearic acids to form a mixture of compounds of the formulae shown:

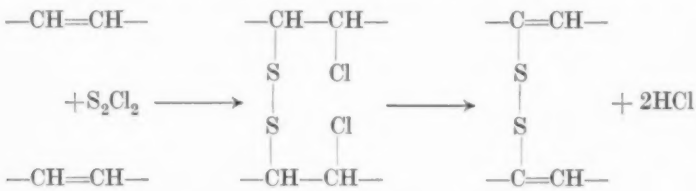


or



Aluminum alkoxides can serve the same purpose. In the case of alkyd and oleoresinous vehicles, small quantities increase viscosity considerably (ARCHER-DANIELS-MIDLAND, unpublished) by reaction with groups containing active hydrogens.

The reaction of sulphur chloride with oils has been known for a long time. There has been limited practical use. Sulphur chloride-treated oils increase in viscosity and have better film characteristics than non-treated oils. It is postulated that the sulphur acts as a bridge between two molecules as follows:



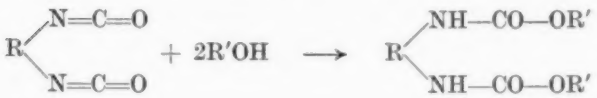
SLANSKY (1952) recently provoked renewed interest in this reaction. He explains the improvement on the basis of modern electronic concepts of chemistry.

2. *Organic compounds*

*iso*Cyanates are by far the most important organic compounds used as cross-linking agents. For the purposes of this discussion, *iso*cyanates and *iso*thiocyanates are considered as equivalent. *iso*Cyanates react with compounds containing active hydrogens such as carboxyl, hydroxyl and amine groups. Both mono- and di-*iso*cyanates are available and have been investigated as oil modifiers. Interest has centered largely on the di-*iso*cyanates and the possibility of using them as cross-linking agents to increase the viscosity of oil based products or alkyd resins. The reaction of an *iso*cyanate with a hydroxyl group to form a urethan is as follows:

$$RN{=}C{=}O + R'OH \longrightarrow RNH{-}CO{-}OR'$$

It is readily seen, that a difunctional *iso*cyanate can react with groups on two different molecules and serve as a cross-linking agent between them, thus;



This is the principle that is used in adapting this reaction to oil chemistry. The products are sometimes referred to as 'Urethan oils'. Greater molecular sizes can be built up by using more functional *iso*cyanates such as the tri- and tetra-*iso*cyanates.

It is not the purpose of this section to review all the possibilities for using *iso*cyanates. A review of newer uses has recently appeared (STAFF REPORT, 1953b) and therefore only a few typical cases are considered.

Preliminary work on the *iso*cyanate oil reaction was carried out in Germany (PUBLICATION BOARD REPORT). Chemists at I. G. FARBEN (1940, 1942) showed that esters containing a free hydroxyl group were reactive with *iso*-cyanates. This work was later enlarged (I. G. FARBEN, 1943) to include partial esters of polyfunctional alcohols and unsaturated fatty acids, and dibasic acids. The *iso*cyanates ranged from the mono- to tetra-*iso*cyanates. (PUBLICATION BOARD REPORT.)

PRATT and ROTHROCK (1944) showed that various varnishes could be reacted with decamethylene *iso*thiocyanate. ROTHROCK (1942, 1945a) also disclosed that the formation of urethans could be accelerated by the addition of 0·2 per cent of cobalt drier. Lead and manganese, as naphthenates or linoleates, were also effective. CASS (1952) has shown that the di-*iso*cyanate castor oil reaction product can be polymerized with styrene to form a series of soluble liquid products which can be converted to solid, insoluble, non-fusible products. The castor oil *iso*cyanate reaction product *per se*, according to ROTHROCK (1942, 1945a) can be used as a plasticizer.

MILLER and PRATT (1948) disclose that poly*iso*cyanates of elements of Groups IV and V of the Periodic Table, (silicon and titanium, for example) will react with monomers or polymers containing active hydrogens. A variety of varnishes, oils and polyesters can be made for use as fibres or film formers.

Among the commercially available *iso*cyanates are toluene 2,4-di-*iso*cyanate, hexamethylene di-*iso*cyanate, and *p,p'*-di-*iso*cyanato diphenyl methane.

Because of cost, *iso*cyanates have been used to only a limited extent for modification of oils and varnishes. The viscosity increase obtained by the use of *iso*cyanates can usually be gained more economically by further processing or other slight modifications. Furthermore, films containing nitrogen derivatives show the disadvantage of embrittlement with age. However, at present, *iso*cyanates are enjoying a very good reception in the polyester and foam rubber fields. Here, again, they are used as cross-linking agents. Their use and the patents covering the latter are described in a recent article (ANON, 1954b).

Several other organic compounds can be used as cross-linking agents. It has been disclosed recently that dicyandiamide, (SCHMUTZLER, 1953) melamine, or other polyamino compounds can be treated with tall oil followed by reaction with aqueous formaldehyde to produce low-cost film formers and impregnants

(SCHMUTZLER, 1952). The monomer N,N′-methylene *bis*-acrylamide has also been mentioned as a cross-linking agent (AMERICAN CYANAMID CO., 1949).

B. Acetylation of Oils

RHEINECK (1940) found that treatment of oiticica oil with acetic anhydride led to markedly improved drying characteristics. The film integrity was greatly improved and the speed of drying was very noticeably increased.

NESSLER and PENOYER (1947) showed that the drying properties of linseed oil could be upgraded to approximate those of a dehydrated castor oil by bodying in the presence of acetic anhydride vapours at about 260°C. SORENSON (1942) conducted the acetylation of linseed oil in the presence of kerosene and acetic anhydride.

The drying properties of China wood oil were also improved by acetylation according to NICHOLS (1950). Mixtures of China wood oil with soybean, linseed and dehydrated castor oil showed similar improvements according to KASS and NICHOLS (1950).

The data in Table 24 show the beneficial effect on drying times produced by the acetylation process.

A somewhat similar effect on drying characteristics can be obtained (RHEINECK, unpublished) by blowing ketene through various oils. This beneficial effect is especially noticeable in the case of oiticica oil. It is possible that the natural inhibitors that are present are acetylated. It was observed in the case of oiticica oil, either ketene-treated or acetylated, that the saponification value increased. This was not the case with soybean, linseed, dehydrated castor and China wood oils.

Acetylation also aids in air blowing of oils. A combination process has been described by KEENAN (1951) in which the oxidation of an oil is accelerated by blowing it with ketene or a mixture of ketene and dry oxygen.

MILLER and SORENSON (1949) treated fatty acids with acetic anhydride at 260°C to produce fatty ketenes which showed drying properties.

X. OTHER DEVELOPMENTS

A. Norepol process

In the early days of World War II when it became apparent that natural rubber would be relatively unavailable attempts were made to find substitutes made from naturally occurring domestic raw materials. Among the latter soybean oil was considered to be a likely contender. It was pointed out by W. J. Sparks in 1942 at the Northern Regional Research Laboratory of the United States Department of Agriculture that soybean oil could be converted to a rubber base material by a series of reactions described in detail by COWAN *et al.* (1945, 1946, 1948) as follows:

(a) Soybean oil is converted to methyl esters plus glycerol by reaction with methanol and basic catalyst.

(b) The methyl esters are heat bodied at 300°C in the presence of anthraquinone.

Table 24. Effect of acetylation on the drying time of various oils

Treated	*Untreated*	*Treated*	*Untreated*	*Drying time*	*Reference*
70% China wood	—	30% Dehydrated castor	—	75 min	Kass and Nichols (1950)
70% China wood	—	—	30% dehydrated castor	150 min	
50% China wood	—	50% soybean	—	150 min	
50% China wood	—	—	50% soybean	180 min	
30% China wood	—	70% linseed	—	150 min	
100% China wood	—	—	—	30 min	Nichols (1950)
—	100% China wood	—	—	360 min	
—	—	100% linseed	—	130 min	Nessler and Penoyer (1947)
—	—	—	100% linseed	230 min	
—	—	100% dehydrated castor	—	115 min	
100% oiticica	—	—	—	20 min	Rheineck (1940)

(c) The bodied esters are separated into dimer and monomer fractions by distillation.

(d) Dimer methyl esters are converted to glycol dimer polyesters by interchange with ethylene glycol and a catalyst.

(e) The dimerized fatty acid glycol polyester is then treated with sulphur and carbon black, mixed on a rubber mill, cured and subsequently vulcanized.

Although several lots of rubber made from this base material were evaluated in automobile tires none was produced on any more than an experimental scale because of the strict allocation of soybean oil for edible purposes.

B. Dimer acids

The results of the Norepol investigation aroused interest in dimerized methyl esters, which have served as a source of dimerized fatty acids, sometimes erroneously termed 'dilinoleic acid'.

Dimer acids were first produced commercially as a by-product in the preparation of oleic acid. Increased demand necessitated other methods of preparation. They are now prepared commercially by direct polymerization of unsaturated fatty acids as described by GOEBEL (1949, 1953). Another method is disclosed by PERCY and ROSS (1944) who prepared polymeric acids by heating soaps of unsaturated acids in the presence of sodium carbonate, followed by treatment with mineral acids.

Dimer acids are used in the preparation of various types of non-phthalic alkyds to help improve flexibility and increase viscosity (HERCULES POWDER Co., 1952; TERRILL 1953a). FALKENBURG *et al.* (1945) and FALKENBURG and COWAN (1951) reacted dimer acid with various diamines to form a series of polyamides. These compounds have found use as modifying agents in protective coating materials, and are now produced commercially. A special use for polyamides of dimer acids is described by WINKLER (1953), who introduced them into alkyd resin compositions to produce thixotropy in vehicles.

According to GREENLEE and ZECH (1950), they can be inter-esterified with acetates of diphenols by acidolysis. The products possess drying properties and are useful in varnish compounds. They can also be converted to vulcanizates by treatment with rubber vulcanization agents.

C. Plasticizers

Blown linseed and soybean oils have been used as plasticizers for nitrocellulose coatings. With the advent of vinyl plastics and their tremendous production the demand for plasticizers increased greatly. A consideration of the chemical properties of vinyl plastics led chemists to see possibilities of using naturally occurring glyceride oils as starting materials for plasticizers.

SWERN (1953) showed that the olefinic unsaturation in drying and semi-drying oils could be epoxidized quite readily. The introduction of an oxirane group markedly increases compatibility with vinyl plastics. Epoxidized soybean oil is compatible with vinyl acetate polymers. The preparation and use of this type of plasticizer is disclosed by TERRY and WHEELER (1949, 1951). Peracetic acid is formed by reaction of hydrogen peroxide with acetic acid in the presence of sulphuric acid. Reaction of peracetic acid with oils leads to introduction of the epoxy group. Epoxidized soybean oil and other oil derived esters are now produced commercially and used to plasticize various types of vinyl resins.

Several other oil-based vinyl plasticizers have also been described. MYERS and WEBSTER (1949) describe the preparation of partially blown short chain alcohol esters of fatty acids. Specifically, *iso*butyl oleate blown to an iodine value of less than 20 is said to be compatible with vinyl resins. DEBACHER (1948) describes the plasticizing properties of a blown 9, 12-octadecadienoic glycerol ester with polyvinyl–butyral type resins.

Mixed fatty acid acetoglycerides are also plasticizers. They are made by alcoholizing a semi-drying or drying oil with glycerol to form what approximates a monoglyceride in composition. The remaining free hydroxyl groups are then acetylated. According to MAGNE and MOD (1953) these esters are good

secondary plasticizers and act as extenders for the more expensive primary plasticizers.

D. Fatty amides

The introduction of nitrogen as an amine, amide or nitrile group into protective coating materials generally increases final film brittleness. Therefore the use of such nitrogen derivatives has been limited. The polyamide from the 'Norepol' process has been described. The literature also describes other amides prepared from drying oil materials.

Bradley (1945b, 1951) prepared a diamide from China wood oil methyl esters and ethylene diamine. He also prepared the amides of linseed acids and 2,4-diamino-2-methyl pentane using xylene as the azeotrope. This product is described as being alcohol soluble whereas the ethylene diamine product is not.

E. Drier developments

Wheeler and Vanderbilt (1951) proposed the use of phenanthroline and α-α-dipyridyl as catalysts to effect air drying of oils in place of the conventional lead and cobalt driers. It is suggested that these be used with manganese drier instead of lead and cobalt. Kaufmann and Korfhage (1953) and Kaufmann and Strüber (1952) describe the use of free radicals of the type of triphenyl-methyl and tri (*p*-phenyl-phenyl) methyl as driers for China wood oil. They state that these compounds must be used in conjunction with a trace of oxygen to effect the reaction.

Vogel (1951) indicates that the drying properties of oils can be improved by air blowing in the presence of driers. It is stated that this destroys the naturally present oxidation inhibitors without changing oil constants. Schlenker (1952) claims that the drying properties of linseed, dehydrated castor and soybean oils, as well as alkyd resins, can be enhanced by treatment with small amounts of aluminium alkoxides. It is stated that this treatment reduces the tack and increases the water-resistance.

Recently Coffey *et al.* (1953, 1954) have shown that compounds soluble in mineral spirits, such as aliphatic and aromatic aldehydes and ketones will act as driers in lieu of the conventional metal driers. They present data showing the effect of octa-decenyl aldehyde, 2-ethyl hexaldehyde, *n*-decyl aldehyde, 3,5,5-trimethyl hexaldehyde, citronellal, cinnamic aldehyde, β-methyl-umbelliferone, *p*-hydroxybenzaldehyde, *p*-hydroxypropiophenone and others on the drying of different alkyd and oleoresinous vehicles of varying oil lengths. Their data show that these organic driers are better in some instances than the conventional metal driers.

XI. Summary

The technology of drying oils during the period, 1935 to 1955, has been discussed in this chapter. The pattern has been not unlike other technological developments during these years. The inter-relationship of drying oils with new developments in other fields, the appearance of new chemicals, and increased availability and lower prices of existing chemicals is quite obvious.

The first approach in these developments was to modify oils *per se*. This work produced isomerized oils and dehydrated castor oil. The latter has found a place in alkyd resin technology, whereas the former have not gained acceptance. Other related oil modifications were of academic rather than technological interest.

Maleic anhydride, pentaerythritol, styrene and its homologues, and aliphatic olefins as materials for the modifications of oils have definitely found their place in present-day oil technology. It is the reaction products of these compounds with oils that have displaced the China wood oil and oleoresinous varnish systems.

The family of pentaerythritols have had a very favourable acceptance in oil chemistry. The technology of their production, as compared with that of other polyols, was sufficiently far advanced at the time when there developed a need for alcohols more functional than glycerol, to permit their use with drying oils. This fact together with their ease of reaction and handling, and the properties imparted to the final products, has led to their large-scale acceptance.

An alternative method of upgrading oils involves the reaction with maleic anhydride. The use of this chemical in other fields necessitated increased production facilities, which made it economically advantageous for use as an oil modifier. As related to oil chemistry, the technology of maleic anhydride closely parallels that mentioned for the pentaerythritols.

The use of styrene with drying oils is relatively recent by comparison with the pentaerythritols and maleic anhydride. This is another instance in which a large-volume production of a commodity for another field, specifically for synthetic rubber in this case, has made its use feasible with drying oils. The extreme interest in styrene–oil copolymers has led to the preparation of styrene homologues for improved ease of reaction and end use characteristics.

Aliphatic olefins, *cyclo*pentadiene, butadiene and their homologues are the result of advances in the field of petrochemicals and synthetic rubber. The development of uses of these compounds with drying oils parallels that of styrene.

It is quite obvious that one of the more important requisites for the use of a new compound is availability in large volume at suitable price. A large number of oil developments have been discussed in this chapter, but in spite of the technical merits of most of them, few have found application because of the absence of the requisites just mentioned.

The future course of drying oil technology is difficult to predict. The pattern to date indicates that it will be closely related to chemical advances and technology in other fields, New compounds are constantly appearing. It is fair to conclude that some of these will find widespread application to an extent as great as some of these already discussed.

Acknowledgement

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9

TECHNOLOGY OF EDIBLE ANIMAL FATS

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9

TECHNOLOGY OF EDIBLE ANIMAL FATS

W. C. Ault

I. Introduction

The edible animal fats, aside from butter, are by-products of the meat packing industry. They may also be referred to as meat fats. Lard and 'rendered pork fat' are obtained from hog-slaughtering operations while edible tallow and certain derived products such as oleo oil are obtained from the carcasses of cattle and sheep.

Lard is by far the most important of these fats in an economic sense in the United States, production usually being in the range of $2\frac{1}{2}$–3 billion pounds per year. Production of each of the other edible animal fats seldom exceeds a few million pounds per year. Production of rendered pork fat has remained so small that for statistical purposes it is usually included with lard. From the legal standpoint, however, they have been separate entities since 1940. Since that time regulations of the U.S. Department of Agriculture have defined lard and rendered pork fat which is produced in federally inspected establishments.

A. Animal fat definitions

Lard. The fat rendered from fresh, clean, sound fatty tissues from hogs in good health at the time of slaughter, with or without lard stearine or hardened lard. The tissues do not include bones, detached skin, head fat, ears, tails, organs, windpipes, large blood vessels, scrap fat, skimmings, settlings, pressings, and the like, and are reasonably free from muscle tissue and blood.

On 9 February 1945, a modifying and interpretive memorandum was issued providing that fresh, clean, sound fat obtained in the fleshing of fresh pork skins may be used in the rendering of lard. It was further provided that fresh ham skins, fresh pork shoulder picnic skins and the like may be used in the rendering of lard when, taken as a lot, they have at least 65 per cent trimmable fat.

Rendered pork fat. The fat other than lard, rendered from clean sound carcasses, parts of carcasses, or edible organs from hogs in good health at the time of slaughter, except that stomachs, tails, bones from the head and bones from cured or cooked pork are not included. The tissues rendered are usually fresh, but may be cured, cooked, or otherwise prepared and may contain some meat food products. Rendered pork fat may be hardened by the use of lard stearine and/or hardened lard and/or rendered pork fat stearine and/or hardened rendered pork fat.

The production of rendered pork fat usually does not comprise more than a few per cent of the total amount of hog fat rendered in federally inspected establishments. In fact, rendered pork fat seldom if ever appears as such on the retail market, being almost entirely used in the manufacture of shortenings or other trade-named items. It should be noted that rendered pork fat is not necessarily inferior to lard. Because the use of fats trimmed from cured cuts is permitted, it will frequently be a little darker in colour and higher in free fatty acids than lard; on the other hand its stability may frequently be higher than that of lard.

B. Pre-rendering care

The production of animal fats having the highest possible quality begins even before the rendering process. Studies reported by VIBRANS (1949) of the American Meat Institute Foundation Laboratories have shown that enzymatic changes taking place in the tissues give rise to development of free acidity in the fat. This hydrolytic change is reduced at low temperatures and hence if tissues are to be kept for a prolonged period before rendering, refrigeration is desirable. Approximately 0·2 per cent free fatty acids developed in leaf fat held at 72–74°F in 24 h while only about 0·05 per cent developed over the same period when the fat was held at 40°F. Killing fats, particularly visceral fats, contain more hydrolytic enzyme than leaf fats and hence their refrigeration before rendering is even more important if free fatty acid development is to be minimized.

II. RENDERING

The term rendering is most frequently applied to treatments designed to remove all or most of the fat from fatty animal tissues by processes which are basically thermal in character. The exact procedure to be followed will be indicated by the nature of the fatty stock, to some extent by the characteristics desired in the rendered fat, and, of course, primarily by the rendering equipment available.

Rendering processes may be classified in a number of different ways. For example, if water or steam is added in substantial amounts prior to or during the rendering, the process is referred to as being a wet process; otherwise, any process may be referred to as being of the dry type.

Rendering processes may be further differentiated upon the basis of the temperature attained during the operation. A further classification of rendering processes may be made upon the basis of the use of additional agents other than heat. Such agents include mechanical action and caustic or enzyme digestion of the proteinaceous tissue. Still another type of operation involves the use of an agent known to have adsorptive qualities in what otherwise would seem to be conventional rendering operations.

A. Dry rendering

Open-kettle rendering was undoubtedly the first type of rendering to be used in packing houses. It represented merely a modification of the rendering methods used on the farm before the development of the meat packing industry.

Gradually the equipment was improved and at present steam-jacketed kettles equipped with stirring devices are commonly used. As customarily practised, open-kettle rendering is a dry-rendering process. Relatively high temperatures of the order of 230–240°F are usually attained. In plants having other types of rendering equipment available, open-kettle rendered fats may be produced from those tissues that are most easily rendered such as the leaf fats. In many small plants, including almost all locker plants doing custom butchering, however, all fresh fats are hashed and rendered in an open kettle. In general, however, the total commercial production of conventional open-kettle rendered fat is relatively small when compared with the total production of edible animal fats in the United States.

Dry rendering may be carried out in equipment other than the simple open kettle. In fact, the open-kettle method is so slow and inefficient that it is not often used for large-scale rendering. The large-scale dry rendering of fats is now usually conducted in closed tanks which during at least a portion of the rendering period may be maintained under reduced pressure. Vacuum-rendering equipment for vacuum dry rendering is frequently referred to as a dry melter. It usually consists of a horizontal steam-jacketed cooking tank equipped with charging door, vent line, vacuum line, discharging door, sampling device and a stirring arm. Merkel (1936) has described a typical batch dry melting unit. Continuous dry melting systems have also been devised.

Efforts to improve the dry-rendering process continue. A recent United States patent describes a process (Hormel, 1949) involving the fine hashing of a fat which is subsequently heated and discharged into a vacuum chamber where moisture is removed. Still another attempt to devise a process capable of yielding a high-quality lard is described by Pavia (1950). This might aptly be described as a low-temperature kettle-rendering process.

Swift and Hankins (1952) have described the results which they obtained during their investigation of the low-temperature open-kettle rendering of lard. In their experiments, leaf fat and skin-free cutting fats were used. A grinder capable of being adjusted to give a hashed fat of different degrees of fineness was used. The rendering was accomplished in a stainless kettle of 20 gal. capacity equipped with a steam jacket around the bottom and lower half of the vessel. Efficient mechanical agitation at 1,725 r.p.m. was provided.

Yields of rendered fat tended to be below desirable commercial levels in their experiments. Under optimum conditions, however, yields averaged 96·0–98·0 per cent, based on the fat content of the tissues, with cutting and leaf fats. They found that the degree of subdivision attained during grinding the fatty tissues markedly affected yield, the best yields resulting from the finest grinds. Highest yields were obtained when rendering tissues which had been cooled to 0°F and ground through a 0·125 in. plate. On the other hand these investigators did not find variations in the rate of heating during rendering nor the temperature of rendering, over the ranges studied, to be critical. The lard rendered at low temperatures had a good colour and a relatively mild odour and flavour. The stability of the resulting lard was acceptable but not

outstanding, averaging about 6 h as measured by the so-called Swift test (King *et al.*, 1933). The moisture content of the lard rendered by these investigators tended to be high but they found that the production of lard having an acceptably low moisture content was possible provided a prolonged period of contact between the lard and the proteinaceous residue was maintained.

Reference to the patent literature indicates that a type of processing which involves the combined use of heat and a solvent has been investigated during the past few years. Thus Leaders (1950) has described the rendering of fats by a process involving treatment of the tissue at a temperature of 160–190°F for about 5 h in the presence of a hydrocarbon such as propane. Sufficient pressure is maintained to keep the solvent in the liquid state. Worsham and Levin (1950) have described a process involving the use of a fat solvent such as a halogenated hydrocarbon for the simultaneous desiccation and defatting of wet organic tissue.

Other approaches to improvement of the rendered fats are based upon contacting the fat with an adsorptive material during the rendering process. Libby and Henderson (1948) have described a process in which the fatty tissue is rendered in conventional manner in the presence of silicic acid; any agent containing or capable of furnishing hydrated silica may also be used. The process seems to be directed chiefly towards use on inedible stock.

The so-called drip-rendering process combines the rendering operation with a carbon treatment into a single piece of equipment in a unique manner. The fat is charged into a rendering tank with a false bottom through which the lard drains away as soon as it separates from the tissues. In this way, time of contact between the hot fat and tissue is minimized. The melted fat may then be mixed with carbon in the lower part of the tank.

B. Wet rendering

Wet rendering is carried out by heating the fatty tissues in the presence of water. Low-temperature wet rendering has been used to produce a fat having a very mild flavour. Only the simplest apparatus is required usually consisting of an open tank equipped with a slow-speed agitator and suitable steam-heating provisions. Variable temperatures below 210°F are employed, and the blandest products are obtained by operating at the lowest possible temperature. Low-temperature wet rendering does not result in a satisfactory recovery of the fat, and the tissues are usually rendered again by a more effective process. This inefficiency combined with the shrinking outlet for animal fats in oleomargarine has resulted in decreasing use of low-temperature wet rendering processes.

Most of the lard and tallow produced in the United States today, however, is steam rendered. Lard so produced is handled on the Board of Trade and is known as 'prime steam lard'. The relatively simple and inexpensive equipment required, its ease of operation and control, the almost complete recovery of fat obtained, and the adaptability to the widest possible variety of stocks combine to make steam rendering relatively attractive for operations of any

magnitude. On the other hand, the expense of evaporating large amounts of water to recover non-fatty residues, and hydrolysis of fats during steam rendering with consequent lowering of smoke point are important disadvantages of the process.

Deatherage (1946, 1949) has described an interesting rendering process which involves the use of dilute caustic in producing lard and other animal fats. In this process the raw fat is ground through a $\frac{1}{8}$ in. plate and mixed with up to half its weight of 1·75 per cent caustic soda solution. With high-quality fats somewhat less solution may be used, about 40 per cent being suggested for back fat and 25 per cent for leaf fat. The caustic solution may also contain 2–5 per cent of dissolved salt. After thorough mixing with caustic brine the whole is heated with atmospheric steam to 85–95°C for 45–60 min. The fat layer is then separated and washed first with brine and then water by centrifugation. A final acid wash as with 0·5 per cent phosphoric acid is stated to improve the flavour of the final product. Bones cannot be processed, but sweet pickle fat is reported to give a high-quality lard by the alkali process. The process also works quite well on beef tallow.

The lard from the caustic process was reported to have excellent characteristics including low free fatty acids (0·01 per cent); a smoke point of 450–480°F; good colour and mild odour. The product had satisfactory keeping quality, was stable to reversion and responded to the addition of antioxidants. It was also readily plasticized and easily deodorized. Deodorization of 400 lb of the resulting lard was accomplished by heating it to 400°F for 4 h during which it was blown with 14 lb of 420°F steam at 3–5 mm of mercury. The yields of lard from various tissues were generally satisfactory and comparable with those of other processes.

Types of fat rendered	*Range of yield per cent*
Ham	72–82
Back	79–90
Leaf	89–93

Several different procedures involving the use of proteolytic enzymes in the rendering of animal fats have been proposed during the past decade. Thus Keil (1947) suggests the use of a proteolytic enzyme in fat which has had its pH adjusted to between 6·0 and 7·5. The resulting mixture is then heated to about 140°F. This inventor reports plant enzymes (papain or ficin) are superior to animal enzymes such as trypsin and pepsin.

Halmbacher (1950) has claimed the use of an enzyme such as papain or ficin with a cysteine activator. This combination reportedly reduces digestion time and increases yield. A report (Anon. 1946) on the use of enzymes concluded that such use seems most promising for locker plant operators and other small meat-processing establishments using the open-kettle rendering process. In general, improved yields of fat were obtained in shorter rendering time, but definite overall economic advantages appeared to be lacking.

A continuous steam rendering process frequently referred to as the Titan Process has been developed in Denmark. A Canadian installation of the process has been described (ANON. 1949). In the Canadian plant, inspected fat is fed into a steam-jacketed grinder from which it passes into a pre-heater consisting of a horizontal cylinder with an internal rotating conveyor drum. At a temperature of about 176°F the fat then goes into an upright pressure boiler where it is subjected to live steam at a temperature in the range of 240–247°F. Under these conditions it rapidly changes into a mixture of water, cracklings, and melted fat. After a rapid release of the pressure, which causes further disintegration of the fat-bearing tissue, the mixture is discharged into a rotary screen. Here the solids are separated and moved into a mechanical screw press which extracts much of the residual fat. The fat–water mixture is further purified by contacting with fresh water and by centrifuging. The complete extraction process requires only 12–15 min from fat to finished lard, and the material is under heat process for only 3 min. The equipment may be used for rendering tallow as well as lard. High-quality fats are produced which are low in acid and moisture and almost neutral in flavour.

An attempt to eliminate entirely the undesirable effects of thermal action on fatty tissues has resulted in the CHAYEN or impulse method of rendering (CHAYEN and ASHWORTH, 1953). The process consists in the mechanical rupturing of the membranes of fat-containing cells by a series of high-speed impulses transmitted through the medium of liquid. The process seems to work quite well for the removal of fat from such material as bones which have a rather rigid structure. To date, however, attempts to adapt the process to the removal of fat from the softer fatty tissues do not seem to have met with commercial success in the United States.

III. USE OF ANTIOXIDANTS

A. Natural antioxidants

Despite all efforts, improved rendering methods have not proved to be the panacea which would make the animal fats entirely competitive with the vegetable fats, on a quality basis. The properties which have remained open to improvement in animal fats are keeping quality or stability, odour, flavour, colour, smoke point and physical characteristics such as plastic range, consistency and creaming power. Although rendering conditions undoubtedly affect the quality factors noted above, except those that involve physical characteristics, the resulting products still have fallen far short of their competitive goals. For example, although careful rendering results in lard having good stability, i.e. 6–10 h A.O.M. value, even the best products do not adequately meet the need for shortenings which can be stored in the home at room temperature during use.

Stability is, in a sense, the key which opens the door to further improvements. Without good keeping quality, the application of other techniques have little value, because the best shortening is unfit for use if it is prone to rancidity.

Numerous investigators have contributed to the now well established opinion that animal fats contain little effective natural antioxidant. The literature on the subject has been reviewed by RIEMENSCHNEIDER (1955). HANSON *et al.* (1944) reported tocopherol to be the only antioxidant out of a considerable number included in test diets which was deposited in the adipose tissues of animals to any appreciable extent. Tocopherol seems to be the principal natural antioxidant in hog fats, being present to the extent of about 1–3 parts per 100,000 (CHIPAULT, LUNDBERG and BURR, 1945). In contrast the principal vegetable oils contain much higher percentages, reaching proportions of nearly 500 parts per 100,000 in wheat germ oil. The antioxygenic properties of pure tocopherols and tocopherol-rich concentrates have been extensively investigated (GOLUMBIC, 1943; BAILEY *et al.*, 1943; GRIEWAHN and DAUBERT, 1948; GYORGY and TOMARELLI, 1944; MITCHELL and BLACK, 1943; OLIVER, SINGLETON and BAILEY, 1944; RIEMENSCHNEIDER *et al.*, 1944a; SINGLETON and BAILEY, 1944; SWIFT, ROSE and JAMIESON, 1942).

Information regarding the occurrence of tocopherols and detailed knowledge of their protective antioxidant action in fats have contributed to the explanation of several observations formerly regarded as being anomalous. For example, it is now readily apparent that unless considerable care is exercised in rendering animal fats, the minute amount of tocopherol present may be destroyed, thereby reducing the stability of the fat to a very low order. In a similar manner the work has shown why addition of tocopherol or a phenolic antioxidant to animal fats is relatively much more effective in increasing stability than similar additions to vegetable fats.

Extensive efforts were directed towards the isolation and identification of antioxidants from natural edible sources on the logical assumption that the addition of such substances to foods prone to rancidity might be permitted. Patents claiming certain aspects of the use of tocopherols were issued (TAYLOR and JAKOBSEN, 1941; EASTMAN KODAK CO., 1939; BAXTER and JAKOBSEN, 1942; ANDREWS, 1941).

Since isolation or even concentration of tocopherols proved difficult and expensive, various proposals to utilize their antioxidant properties without such steps were made. Workers at the Eastern Regional Research Laboratory reported (RIEMENSCHNEIDER *et al.*, 1944) that addition of 1–10 per cent of certain tocopherol-containing vegetable oils or of corresponding vegetable oil shortenings to lard increased the stability from two-fold to five-fold. MAGOFFIN and BENTZ (1949) reported that potato chips fried in a mixture of equal parts of lard and vegetable shortening were nearly as stable as those fried in vegetable shortening alone. Other publications (LIPS and MCFARLANE, 1943; RIEMENSCHNEIDER and AULT, 1944; ANZALDI, 1948; THALER and SCHOTTMAYER, 1942), confirming these reports have appeared and patents have been issued describing mixed shortenings (ALDERKS, DISTEL and TAYLOR, 1935; GRETTIE, 1936, 1940; GRETTIE and NEWTON, 1934; MEHLENBACHER, 1938; NEWTON and RICHARDSON, 1932).

Vegetable lecithin, another component of vegetable oils, received early

consideration as an antioxidant. Its potential use was facilitated by a process for its isolation which was first proposed by BOLLMANN (1923). It is obtained chiefly as a by-product of the manufacture of soybean oil and corn oil as an extremely complex mixture containing lecithin, cephalin, phosphoinositides, sugars, sterols, glucosides, pigments and tocopherols. It is available in large quantities and at nominal cost.

Numerous investigations have been made of its antioxidant action in fats, even though the origins of this specific use seem vague. There appears to be some doubt, however, whether lecithin should be regarded as a primary antioxidant. Any slight primary antioxidant activity which it shows may be assigned to other antioxidants such as tocopherols present in small amounts.

Other fats and oils have been found to have components present which confer stability upon them. Probably the most notable example is the presence of sesamol in sesame oil. Naturally these oils as well as the antioxidant fractions contained in them have been investigated for use in the stabilization of lard.

Following early investigations which pointed to the chemical nature of natural antioxidants occurring in many vegetable oils, numerous attempts were made to find natural materials which would be rich in similar substances. In view of the work of MOUREU and DUFRAISSE (1922, 1923, 1926), particular attention was given to natural substances relatively rich in complex phenolic materials.

Work along these lines eventually proved fruitful; thus guaiac resin became the first substance of non-food origin permitted as a preservative for lard and rendered pork fats in the United States. This permission was granted on 26 December 1941. This resin, a secretion of a tropical evergreen tree, *Guaiacum officinales*, indigenous to the West Indies, was first proposed as an antioxidant for fats by NEWTON and GRETTIE (1933). Gum guaiac contains complex phenolic constituents to which it presumably owes its antioxidant value.

Nordihydroguaiaretic acid (NDGA) is a phenolic compound which was isolated from a natural non-food source. It is obtained by extraction from the desert plant *Larrea divaricata*, one of a group of plants commonly known as creosote bush. It grows wild in desert areas of south-western United States. LUNDBERG *et al.* (1944) first described its antioxidant activity; its use as an antioxidant was patented by LAUER (1945) and the patent assigned to the Secretary of Agriculture.

Other naturally occurring materials which have been studied at various times include the tannins, gallic acid, conidendron and derivatives of the latter such as norconidendron and the α- and β-conidendrols.

B. Synthetic antioxidants

Knowledge of the chemical nature of the active constituents of these materials stimulated efforts toward the development of truly synthetic antioxidants. A large number of compounds were prepared and investigated particularly for use in lard. No complete review of this work is desirable here, but those which have found some acceptance are discussed briefly below.

Hydroquinone shows excellent antioxidant properties as evaluated in lard. Permission to use this compound in lard has been withdrawn, however, in the United States.

The use of propyl gallate as an antioxidant for fats was first proposed in 1941 by SABALITSCHKA and BOEHM. LEA (1944) showed that the methyl and ethyl gallates are also highly effective antioxidants. The higher alkyl gallates were first prepared by MORRIS and RIEMENSCHNEIDER (1946).

The first publication giving detailed information concerning the antioxygenic activity of butylated hydroxyanisole (BHA) in fats was that of KRAYBILL *et al.* (1949). The commercial product consists chiefly of two isomers, namely, 3-tertiary butyl-4-hydroxy anisole and 2-tertiary butyl-4-hydroxy anisole. Of these, the work of ROSENWALD and CHENICEK (1951) has shown that the 3-tertiary butyl isomer is the more effective as an antioxidant for lard.

Another compound of the 'hindered' phenolic type which has received considerable study is 2, 6-di-tertiary-butyl-4-methylphenol (2, 6-di-tertiary butyl paracresol). This compound is frequently referred to as butylated hydroxy toluene (BHT).

C. Antioxidant synergists

Early workers in the field of antioxidants for fats noted that some substances were quite effective for certain fats but much less effective with others. Gradually two distinct groups of 'antioxidants' came to be recognized, those which were quite effective in animal fats but much less so in vegetable fats and those which were relatively more effective in vegetable fats than in animal fats. It was soon noted that phenolic materials and other antioxidants of the type originally described by MOUREU and DUFRAISSE (1922) belonged to the former type. It was usually observed that other materials such as lecithin, phosphoric acid, citric acid and certain other acidic materials were found to function best in vegetable oils or in meat fats to which a phenolic antioxidant had been added.

Substantial evidence that these synergistic antioxidants functioned largely if not almost entirely by metal deactivation was presented by MORRIS *et al.* (1950).

D. Governmental Regulations (U.S.A.)

At present, regulations governing the Meat Inspection of the United States Department of Agriculture provide that, with appropriate declaration on the label, a number of preservatives may be added to rendered animal fat or a combination of such fat with vegetable fat. These preservatives which may be used in the amounts indicated are:

(a) Resin guaiac not to exceed 0·1 per cent; or

(b) Nordihydroguaiaretic acid (NDGA) not to exceed 0·01 per cent; or

(c) Tocopherols not to exceed 0·03 per cent. (A 30 per cent concentration of tocopherols in vegetable oils shall be used when added as a preservative to products designated as 'lard' or as 'rendered pork fat'); or

(d) Lecithin: Provided, that nothing in this paragraph shall prevent the use of this substance as an emulsifier in an approved manner; or

(e) Butylated hydroxyanisole (a mixture of 2-tertiary butyl 4-hydroxyanisole and 3-tertiary butyl 4-hydroxyanisole) not to exceed 0·01 per cent; or

(f) Butylated hydroxytoluene (2,6 ditertiary butylparacresol) (2,6 ditertiary butyl 4-methylphenol) not to exceed 0·01 per cent; or

(g) Propyl gallate not to exceed 0·01 per cent; or

(h) Combinations of two or more of the preservatives listed in sub-paragraphs (b), (e), (f), and (g) above not to exceed 0·02 per cent; or

(i) Citric acid and/or phosphoric acid and/or mono*iso*propyl citrate not to exceed 0·01 per cent, either alone or in combination with the preservatives listed in subparagraphs (b), (e), (f), (g) or (h) above.

(j) Recently dodecyl (lauryl) gallate was made permissive for addition to lard which is to be exported from the United States to the Netherlands.

IV. Deodorization

A. General

As the commercial production of fats and oils increased during the nineteenth century methods for improving the yield from fat- and oil-bearing raw materials were developed. These newer production methods which invariably involved the use of heat generally resulted in products having strong flavours and odours. Frequently these flavours and odours were atypical of those which usually were associated with specific fats and oils and hence were quite undesirable. This led to the need for development of methods for removing the undesirable substances responsible for these unwanted characteristics. The desire for effective means of deodorizing fats was stimulated further by the advent of commercial hydrogenation, a process which imparts an undesirable and characteristic odour and flavour to fat.

The approach to the solution of the problem of undesirable odour and flavour of food fats required careful consideration of the physiology of taste and smell, which is actually quite well defined. The organ of taste is the mucous membrane of the tongue and in some persons, of the soft palate and fauces. In this organ are located the taste buds, each consisting of six or eight taste cells. In order for substances to be tasted they must be in solution. If the tongue is wiped dry and a crystal of sugar is placed on it, no taste will be noted until exuding moisture has dissolved some of the crystal. This fact is especially pertinent with regard to statements occasionally encountered concerning the flavour of fatty substances.

In contrast, the perception of odour depends upon stimulation of the olfactory nerve endings which are located in a small area high up in the nasal passage. The olfactory patches are located somewhat aside from the main channels through which the currents of air pass during breathing. The olfactory cells are stimulated therefore, only by such odorous substances as diffuse to them from the main air currents. By the conscious act of sniffing, however, the air current is directed more nearly upon the olfactory patches, thus effectively enhancing the keenness of smell.

Flavour sensitivity in man is not very great, the sense of smell being much more acute than the sense of taste. This means, of course, that many flavour problems are in reality odour problems, and that elimination of undesirable odours will eliminate in most cases the undesirable flavour, too. Since odours can only result from airborne materials it is logical that steps for removal of all substances having significant vapour pressures will result in practical deodorization.

Early methods for dealing with the problem of unwanted odours and flavours in fats included attempts at masking of odours by means of addition of aromatics, 'washing out' odours with water, and various chemical refining treatments particularly with acid or caustic. LEE and KING (1937), in their paper describing the development of edible-oil deodorizing equipment and methods, point out that the greatest commercial success attended the use of steam stripping. This became particularly true following the description (BATAILLE, 1924) of a steam ejector for the successful maintenance of vacua of 3–8 mm Hg. Names associated with the early development of steam deodorization processes are Rocca, Lurgi, Wecker and Wesson.

The availability of the vegetable oil shortenings completely devoid of any characteristic odour and flavour was followed by their increasing acceptance and favour, particularly by American housewives. Gradually the animal fats such as lard with their characteristic odour and flavour decreased in acceptability. Although the odour and flavour of lard may be desired by some people in certain products such as pie crust, very few wish to have it in a shortening which is to serve a variety of purposes.

In the meantime, considerable effort went into attempts to develop special methods for the manufacture of animal fats having little or no objectionable odour or flavour. In retrospect these efforts to produce a satisfactory bland product from animal fats without a specific deodorization step appear to have been foredoomed. It is hardly to be expected that treatment with adsorbents or mere modification of the rendering process will produce an animal fat so free from characteristic odour and flavour as to meet no objection on this count. Beginning recently, the lard, rendered pork fat or tallow being used in shortening manufacture may also be subjected to chemical processing, such as hydrogenation, which introduces an atypical odour or flavour that must be removed. Occasionally chemical processing such as treatment with sodium methylate may result in products (in this case methyl esters) that are most readily removed by a deodorization treatment. Finally, thorough steam deodorization is an effective way of removing free fatty acids from fats if the percentage present is relatively low. Since free fatty acids are an important factor contributing to low smoke point in shortenings, their simultaneous elimination from shortenings is very worth while. For these reasons steam-vacuum deodorization of animal fats has increased substantially during the past decade. This increase has resulted from a great variety of investigations on numerous aspects of the odour and flavour problem of fats. Numerous laboratory investigations have been reported.

B. Laboratory studies

A simple, all-glass laboratory deodorizer has been described by BAILY and FEUGE (1943). In their apparatus a bulb heated by a so-called heat lamp serves as a source of scrubbing steam. After passage through the heated oil, the moisture is condensed along with entrained materials by two glass traps or condensers containing dry ice. Somewhat later LIPS (1950) also described a relatively simple all-glass laboratory set-up for deodorizing fats. He reported that with a treatment for 1 h at 240°C, he consistently obtained bland oils and shortenings containing less than 0·05 per cent free fatty acids calculated as oleic acid.

SANDERS (1944) in reporting his studies of attempts to predict the flavour stability of soybean oil gave a brief description of the metal deodorizer he used. His unit was constructed of stainless steel, was electrically heated and was capable of handling eight 1 lb samples simultaneously. An all glass laboratory deodorizer capable of being used for the simultaneous deodorization of four samples has been described by SCHWAB and DUTTON (1948). The authors report that they were able to obtain nearly identical conditions of time, temperature, pressure and rate of steam flow on four samples simultaneously by use of the apparatus.

Two different devices for the semi-continuous deodorization of oils in all-glass laboratory equipment have recently been described by Van der Wal and Van Akkeren (1951). One device which they used was constructed from a modified Oldershaw distillation column; the other column used operated on a bubble-cap principle. They found that either column would effectively deodorize an oil even when using steam at the low rate of 0·5 part based on the oil. The simultaneous removal of a substantial percentage of the free fatty acids present is also effected.

A number of investigators have turned their attention to study of the side-effects of steam deodorization. Riemenschneider and co-workers reported (1944a) that deodorization in all-glass equipment in the laboratory produced no appreciable increase in the stability of steam-rendered lard, but significantly increased the stability of kettle-rendered lard. They obtained variable results by deodorization of lard before and after addition of certain antioxidant mixtures. Working with tocopherol-containing fats, BAILEY and FEUGE (1944) found that addition of lecithin or phosphoric acid was usually equally effective whether added before or after deodorization. If such a fat, however, is nearly rancid, these phosphorus-containing materials are much more effective when added before deodorization.

Working with vegetable oils, BALDWIN found (1948) that the amount of volatile substances removed by a laboratory deodorization was usually of the order of 0·2–0·3 per cent. Volatile aldehydes, ketones and alcohols present are removed. Peroxides present are decomposed, and possibly for this reason the stability of deodorized vegetable oils is usually increased. Working with corn oil, soybean oil, and grain sorghum oil, this investigator found that the stability of the oils increases rapidly during the initial part of the deodorization and this increase in stability is caused apparently by the heat-destruction of

pro-oxidants rather than by any removal of volatile materials. These results are in contrast with the report of Robinson and Black (1945), that the stability of animal fats is usually reduced by deodorization.

In many cases the reduction of stability which occurs during deodorization is undoubtedly due to metal pick-up during the treatment. Ziels and Schmidt (1945) by use of metal shavings placed in laboratory deodorizers showed aluminium and nickel to be the only metals examined which were free of any pro-oxidant effect. Lead, manganese, copper, cobalt and iron were the worst metals tested. Of a number of alloys tested their techniques indicated Inconel (International Nickel Co.) and Rezistal (Crucible Steel Co.) were the best. Workers at the Northern Regional Research Laboratory showed (Evans *et al.* 1952) that addition of metal scavengers to soybean oil was quite effective in overcoming the effects of increase in iron content during commercial deodorization.

C. Commercial development

A brief but informative historical sketch of the development of commercial edible oil deodorizing equipment and methods was published by Lee and King in 1937. After discussing the needs for deodorization, they outlined the principal steps in the development of deodorization equipment. Even at that early date they concluded that the trend was toward continuous processes with automatic control. In 1940 Dean and Chapin described the commercial advantages which they had observed during the operation of a continuous deodorization plant over a 2 year period. They claimed marked savings in steam and condensing water by comparison with requirements for batch operation.

Several very excellent treatments of the theory and practice of deodorization have since appeared. Bailey (1941) has discussed losses during deodorization, influence of temperature, absolute pressure, and vessel design, particularly with reference to the mathematical treatment of the theory of distillation by steam. In a paper presented before the Short Course of the American Oil Chemists' Society in 1949 Bates has given a more detailed treatment of the fundamental and theoretical considerations involved in deodorization. A companion paper by Morris (1949) has presented a comprehensive review of the operation from a practical point of view.

Barnebey (1949) in a paper on the high-temperature processing of fats has presented a flow sheet for a typical batch deodorization unit. He makes the very excellent point that, although the degree of removal of free fatty acids from a fat has been widely used as the measure of the extent of deodorization, the correlation is not necessarily a good one. Actually there is no completely satisfactory substitute for sensory odour and flavour tests. Since their description, the panel method for sensory testing outlined by Moser *et al.* (1947) of the Northern Regional Research Laboratory seems to be the accepted standard in this respect.

White (1951) has enumerated seven factors which influence the product obtainable from a commercial deodorizer. These are (a) condition of feed stock,

(b) condition of stripping steam, (c) condition of equipment, (d) materials of construction, (e) method of heating, (f) operating vacuum and (g) length of time involved. Two years later this same author (WHITE, 1953) has written a very good discussion of commercial deodorization. In this article he has presented a great deal of information about a number of the more generally used pieces of American equipment. Cuts are shown of a batch deodorizer with internal heating coils and one with external heating coils, both as designed by Foster–Wheeler; of a continuous deodorizer by the same company and another design by Wurster and Sanger, Inc. Some attention is also given to the semi-continuous deodorizer offered for sale by Girdler Corp. This last piece of equipment has been described in considerable detail by BAILEY (1949).

V. GLYCERIDE REARRANGEMENT

A. Historical

The animal fats have been treated in many ways in an effort to improve their physical properties. Lard, for example, has been blended with other fats and oils, it has been hydrogenated under a wide variety of conditions and it has been fractionally crystallized to achieve such improvement. Moreover, it has been subjected to a wide variety of purely physical treatments frequently referred to as homogenizing, plasticizing or texturizing. Yet none of these steps alone or in combination seem to have entirely eliminated such undesirable characteristics as the tendency to develop large crystals leading to a 'grainy' appearance. Fundamental alteration of the glyceride composition seems to be necessary to achieve this objective. The simplest way to achieve such alteration is by ester interchange.

An ester interchange reaction was first reported by FRIEDEL and CRAFTS (1865). These investigators noted that increased temperature tended to promote the reaction. They reported that upon heating a mixture of equal parts of ethyl benzoate and amyl acetate for 60 h in the temperature range of 200–240°C some amyl benzoate was formed but that the proportion was so small that its isolation was difficult. They further reported that on heating the same mixture for several hours at 300°C in a sealed tube a mixture resulted from which eytyl acetate and amyl benzoate were easily isolated by distillation. The idea that relatively high temperatures were essential to the progress of the reaction was to persist for some time.

NORMANN (1923) seems to have been the first to report the application of the inter-esterification reaction to triglycerides. He reported that by heating tributyrin with tristearin a stearo–butyric glyceride was formed. The following year VAN LOON (1924) described his experiments claiming tin, stannous hydroxide and sodium ethylate to be effective catalysts. Shortly thereafter, GRUN (1925) published further observations on this reaction.

NORMANN (1925) continuing his work described further experiments of interest in a patent which discloses that when mixtures of esters of fatty acids are heated at a high temperature for a prolonged period, with or without a catalyst,

mixed esters having lower melting points are formed. Suitable catalysts included aromatic and aromatic–aliphatic sulphonic acids, tin and its salts, and alkali alkoxides. In light of more recent information one experiment reported is particularly interesting; 20 parts of tristearin and 80 parts of coconut oil were mixed to form a product melting at 57·3°C. When a portion of this was heated for 2·5 h at 250°C with 1 per cent naphthalene sulphonic acid, a product was obtained which melted at 34·5°C. Another portion when heated in vacuo for 0·5 h at 140°C with 0·5 per cent sodium ethoxide gave a product melting at 31·4°C.

Apart from two patents issued to Van Loon (1930, 1932) there seems to be no literature evidence of further activity in this field for more than a decade. It was undoubtedly recognized by these early investigators that the physical properties of a fat could be altered by a reshuffling or rearrangement of the fatty acids on the glyceride molecules. Nevertheless, the rearrangement as carried out at that time involved extremes of time and temperature and hence was undoubtedly accompanied by discoloration and even thermal breakdown of the fat. This discouraged attempts to put the reaction to practical use. Another problem of considerable magnitude and one which must have assumed almost forbidding proportions to the earlier investigators has been that of determination of the glyceride composition of fats. Available methods have been extremely tedious and time-consuming and frequently gave data of an inconclusive nature. Earlier efforts to apply the use of fractional crystallization from solvents to the study of glyceride structure were largely devoted to efforts to isolate pure glycerides.

For a number of years, however, Hilditch and his associates employed the crystallization technique for a somewhat different purpose. A detailed review of the extensive work of Hilditch and his associates in this field is beyond the scope of this paper. Most of his work is summarized in his treatise (Hilditch, 1956) on the chemical constitution of fats. In the method used extensively by his associates the fat was separated by fractional crystallization from acetone at 0°C into several fractions less complex than the original. Each fraction was then examined for its fatty acid composition, fully saturated glyceride content, and content of tri-C_{18} glycerides by determining the tristearin after partial or complete hydrogenation. With this analytical information available, it was possible within limitations, to deduce the approximate glyceride composition of the original fat on the basis of the assumption that the individual fatty acids are distributed as evenly as possible among the glycerol molecules. One of the limitations of this procedure is the inability to differentiate between the various types of mixed unsaturated glycerides, such as stearodioleins and stearooleolinoleins, and stearodilinoleins, which after complete hydrogenation are determined in the form of tristearin.

More recently, Riemenschneider *et al.* (1940) and Hilditch and Maddison (1940) independently found that crystallization at much lower temperatures, —40°C or lower, effects considerable fractionation of the liquid glycerides. From studies based on such low-temperature crystallization,

RIEMENSCHNEIDER *et al.* (1946) recognized that the glyceride distribution in lard which they found was significantly different from random, but thought these differences might well be due to metabolic changes occurring after the glycerides were formed and suggested that the formation by the animal probably followed a random pattern. At about the same time, however, NORRIS and MATTIL (1946, 1947) concluded from their work that animal fats, unlike seed fats, have a random pattern of glyceride distribution.

Somewhat earlier than this, however, the groundwork was being laid for the practical application of glyceride rearrangement to animal fats. Thus BAILEY (1945) in his treatise discloses that he filed patent applications describing the use of a rearrangement process to change the crystal habit of lard. At about this same time GOODING (1943) described his work on the preparation of mixed esters of polyhydric alcohols by use of a rearrangement catalyst plus a material capable of furnishing excess alcoholic hydroxyl groups. As a catalyst he recommended up to 1 per cent of an alkali metal soap and up to 2 per cent of an hydroxyl-containing compound such as glycerol.

Some of the most interesting possibilities in the field of inter-esterification of glycerides have been pointed to by the directed inter-esterification work of ECKEY. His first reported work (ECKEY 1945) in this area describes carrying out the reaction under a fractionating column in such a manner as to remove the lowest boiling fatty component. This was accomplished by rearranging the fatty acid radicals in the presence of ester interchange catalysts, using volatile esters of the acids being introduced. Temperatures above 200°C were usually used for this work. The properties of the non-volatile glycerides were, of course, altered by this treatment.

Several years later (ECKEY, 1948a,b) this same investigator described his work on the development of a process of directed rearrangement carried out in the presence of a rearrangement catalyst at a temperature low enough to permit crystallization of solid triglycerides. Temperatures used were of the order of 0–50°C. Catalysts found useful for the low-temperature work include sodium and potassium methoxides. Sodium triphenyl methyl is also active. Compounds of sodium with material much more acidic than alcohol were not found useful. When the desired degree of reaction had been achieved, the catalyst was usually destroyed by washing with dilute phosphoric acid. If the product was to find edible use, methyl esters formed during the reaction were removed by steam deodorization techniques.

Numerous potential advantages can result from application of the directed process. When a fat is interesterified in a molten state or in solution a completely random distribution of the fatty acid radicals is always approached. When the reaction is carried out under conditions which result in removal of one of the components from the reaction site this same randomization reaction may lead to entirely different results, however. Thus, at low temperatures the reaction equilibrium is altered by removal of the more saturated components by fractional crystallization, thereby leading to products with novel properties.

Interest in rearrangement of fats, particularly lard, was stimulated

considerably by the work of VAN DER WAL and VAN AKKEREN (1951). These investigators reported that a relatively mild treatment of lard with an alkali metal alcoholate improved the product for use in cake baking by increasing the volume. Although lard has been considered to be excellent for use in pie baking, its use as a general purpose shortening was hampered by the fact that it did not produce cakes having a high volume. This deficiency also limited its use in most commercial mix formulations.

B. Present processes

A paper describing the process for lard rearrangement as carried out by Armour and Co. has been published by SLATER (1953). A flow sheet and pictures of the process as carried out in the Kansas City plant of the company are presented. The lard is refined and dried prior to treatment with the sodium methylate catalyst at 175–180°F. Two 5,000 lb reactors are the heart of the process.

HOERR and WAUGH (1955) have discussed the results of their X-ray studies on rearranged lard. They find a generally more diffuse pattern with rearranged lard as compared with ordinary lard, indicating that it possesses a less well-ordered arrangement of its molecules. They also find that whereas rearrangement does not alter the short spacings, the long spacings are increased from 39 to 48 Å. In order to explain the fact that the large crystals characteristic of lard do not form after rearrangement, these authors have hypothesized that in lard close packing is possible, while in rearranged lard imperfect (or extended) packing is more likely. They conjecture that the imperfect packing of the rearranged lard crystals indicates that they possess a somewhat higher free surface energy and consequently they are unable to grow to the relatively large proportions of the ordinary lard crystals.

Quite recently an excellent description of the commercial use of directed esterification as a new processing tool for lard has appeared (HAWLEY and HOLMAN, 1956). Several advantages are claimed for the use of low-temperature directed interesterification. Among those are (a) the higher percentages of trisaturated glycerides formed by directed interesterification eliminate the need for addition of completely hydrogenated fat (hardstock) to lard in order to give it desirable heat resistance and (b) improved plastic range in the resulting product when compared with products made from similar stock by other available procedures.

The initial laboratory work and preliminary pilot-plant work were done batch-wise, but later pilot-plant work led to the development of a continuous process which is used in the commercial unit. The process is described essentially as as follows: lard is pumped first through a vacuum drier and then cooled to a temperature just above its melting point by passage through a heat exchanger. A carefully metered stream of sodium–potassium alloy, the catalyst, is then pumped with the lard into a small continuous mixer where the catalyst is suspended throughout the lard in a finely divided form, 10–40 μ in diameter. The catalysed lard continues on through a scraped-wall heat exchanger in which the temperature is quickly dropped to the point desired for initiating

crystallization of trisaturated glycerides. Stock leaving the cooler goes to a vessel where the reaction proceeds under carefully controlled agitation. The resulting initial crystallization of trisaturated glycerides liberates considerable heat of fusion which leads to the necessity for a second cooling step. After the second cooling the lard passes to a second crystallizer where the precipitation of trisaturated glyceride continues to the desired level. The end point is determined by a cloud-point or solids-content measurement of the stock leaving the crystallizer. When the desired point is reached, the catalyst is 'killed' by adding water, and carbon dioxide is injected with the water to minimize saponification losses. The reaction mass is then warmed to melt the trisaturated glycerides, after which the soap phase is separated from the lard in a conventional centrifuging operation. The lard is then ready for final processing and packaging.

The use of an alloy of sodium and potassium as the catalyst is reported to offer several advantages largely associated with the fact that it can be used in a liquid form. This facilitates pumping and precise metering.

In conclusion it may be stated that glyceride rearrangement is now being practised commercially on lard in the United States to a significant extent. Adequate methods are available for control of the processes, although further developments along these lines may be anticipated. Principal advantages to be hoped for by the glyceride rearrangement operation as applied to lard include:

(a) An improved plastic range in the product.
(b) Greater uniformity in the finished product and a flexibility which permits a wider selection of raw materials; a percentage of cheaper fats such as edible tallow can frequently be used.
(c) Improved appearance due to elimination of graininess.
(d) An outstanding overall baking performance; and finally
(e) Stability against change under market storage conditions.

VI. Summary and Conclusions

The edible meat fats, lard and tallow are almost completely digestible. They are high-energy foods and contain substances neccessary for good nutrition. They are also of great economic importance. Lard production alone in the United States usually exceeds 2·5 billion pounds a year. Edible tallow production, currently below 100 million pounds per year, could undoubtedly be expanded greatly if any economic advantage attended it.

For many years lard was considered to be the outstanding shortening. Because lard has reasonably satisfactory properties, producers have generally been anxious to consider it to be a finished product. Slowly but surely, however, research resulted in improvement of the characteristics of the hydrogenated vegetable oil products until they surpassed lard in a number of important respects. This had its effect in the market place and lard gradually fell into disfavour with many discriminating users. At first an attempt was made to meet this problem by price adjustments, but with the growing level of consumer income this approach did not give completely satisfactory results.

In the meantime research efforts were directed increasingly to the improvement of keeping quality or stability, physical characteristics, odour, flavour, and smoke point of lard and edible tallow. It was recognized early that stability was the key property without which the application of techniques for other improvement would have little value because the best shortening is unfit for use if it is rancid. This problem was vigorously attacked with salutary results. There are now available and approved for use antioxidant combinations which are inexpensive, easily used and quite effective; they have value not only in preserving the fat itself but also in delaying the onset of rancidity in foods which may be prepared from the animal fats. Moreover, these materials have all been found to be free of deleterious results in extensive feeding experiments.

Availability of suitable antioxidants makes feasible the further processing of lard. Subjecting it to modern deodorization techniques is now resulting in products which are essentially odourless and tasteless; moreover, elimination of the free fatty acids which takes place simultaneously effectively raises the smoke point.

In the meantime considerable progress has also been made in improving the physical properties of lard. Whether recently developed techniques such as rearrangement will be the ultimate solution to these problems cannot yet be answered, but the problem is being vigorously attacked and certainly progress has already been made along these lines. Increasingly, lard is coming to be viewed as a raw material which may be used to manufacture shortenings which are very acceptable to the consumer.

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THE TECHNOLOGY OF MARGARINE MANUFACTURE

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THE TECHNOLOGY OF MARGARINE MANUFACTURE

G. B. Crump

I. Introduction

Margarine is a nutritionally acceptable table spread, prepared from an edible fat, with which is intimately mixed cream, milk or skim milk. Congealing is effected, either with or without contact with water, and the congealed mixture may be worked. In the preparation of margarine certain other ingredients may be used, such as salt, artificial colouring, sodium benzoate or benzoic acid, Vitamins A and D, artificial flavouring, lecithin, monoglycerides and diglycerides, butter, citric acid and *iso*propyl citrates (Federal Security Agency, 1951).

II. History of Margarine

The invention of margarine was a result of the serious butter shortage in France during the Franco-Prussian war. Napoleon III offered a prize for the successful production of a fat food which would be as appetizing, as nutritious, and as stable as butter. This prize was awarded in 1870 to the chemist Mège-Mouriés, who had been a pupil of the great Chevreul (Snodgrass, 1930a). Mège's process consisted essentially of four steps; (a) mincing and washing of fresh fat; (b) digestion of the minced fat with artificial gastric juice; (c) expression of the softer portion of the fat from the harder; (d) digestion and agitation of the soft fat thus obtained with milk and mammary-gland tissue extract.

Steps (a) and (c) cannot be considered original. The washing of the minced fat undoubtedly contributed to improving the flavour by removing some non-fatty material. The fractional crystallization of the fat to produce a lower-melting fraction somewhat resembling butter in consistency was not a new idea, for it had been practised for a long time in one form or another in producing hard fat for the candle industry.

Step (b), the digestion of the fat with pepsin, actually was a low-temperature rendering. Whether Mège thought peptic digestion at a temperature not exceeding 45°C produced a chemical change in the fat, or whether he considered it a special method of rendering is not clear; but actually, he established the principle of low-temperature rendering for production of a bland fat free of odour and flavour.

Step (d), the agitation of the fat with milk and extract of mammary-gland tissue apparently was based on the belief that the body fat of the cow was

chemically changed by action of enzymes in the udder into butterfat. This, of course, was erroneous, and the use of mammary-gland tissues was abandoned relatively early. However, the important discovery was made that by churning with milk some of the flavour of butter is produced in the fat.

Snodgrass (1930b) credits Mott in 1877 with the next important improvement, that of preventing graininess by quick chilling. Mott also describes the use of soured milk in the description of his process.

The two economic forces of scarcity and cheapness have largely shaped the course of the development of margarine. In Europe, it was a welcome addition to the scarce supplies of food fats, and margarine has been relatively free of restrictive legislation.

In the United States, however, the situation was different.

The plentiful supply of fats made the manufacture of margarine quite inexpensive. This was an open invitation to the unscrupulous to adulterate butter with margarine, or to sell margarine for butter. Widespread fraud, and the fact that factory-made margarine was considered unfair competition to the 'home' industry of the large number of dairy farmers led to the adoption by the Federal Government of restrictive legislation as early as 1886. Prior to that twenty-two states had already adopted legislation either prohibiting the manufacture or sale of margarine, or regulating the labelling and conditions of sale.

In 1886 the first Federal Act regulating the manufacture and sale of margarine was passed. It provided for manufacturers', wholesalers' and retailers' taxes, a manufacturing stamp tax of 2 cents/lb, and regulations for packing. The bill had no regulations concerning colour.

Because the chief difficulty in enforcement of the law was in distinguishing between butter and coloured margarine, the states began passing laws forbidding the sale of coloured margarine. In 1902 the original Federal law was amended to place a 10 cents/lb tax on coloured margarine, while uncoloured margarine was taxed only $\frac{1}{4}$ cent. Additionally, the wholesalers' and retailers' licenses were substantially reduced if only uncoloured margarine was handled. This is the law, with minor amendments, that regulated the manufacture and sale until 1950.

The original act of 1886 was sponsored by two groups. One of these consisted of those who were genuinely appalled at the amount of adulteration that was being practised in all food manufacture and were in favour of any legislation that regulated such adulteration. The other group represented the butter producers, who were naturally inimical to competition. Apparently very little opposition was presented, although there was some protest from the meat packers who supplied the principal raw material for margarine, and from some labour leaders who thought that it would increase the price of butter.

Again, in 1902, there was some opposition from the southern farmers, who saw an outlet for their cottonseed oil, and from labour leaders; but the northern states were largely anti-margarine, so there was no real opposition to the provisions of the bill.

In the years 1914–34, when margarine was largely made of coconut oil, there was little interest in margarine by any group.

In the early 1930s, during the depression, large surpluses of cottonseed oil accumulated, and there was much unfavourable publicity regarding the use of an imported oil in margarine while the farmers could find no market for their cottonseed oil. This led to the shift from coconut oil to domestic oils, and indirectly to repeal of the tax laws.

During World War II, the shortage of butter led a great many people who had never before used margarine to try it. Thanks to technological advances, they found that they were being offered a product which was an excellent substitute for butter. After the War the continued high price of butter, bolstered by price support subsidies of the Government, caused a great many more people to continue to use margarine.

Meanwhile, the growing use of soybean oil as well as cottonseed oil in margarine aroused the interest of the mid-west soybean growers. The combined interest of the southern and mid-west farmers, plus the acceptance of margarine in place of high-priced butter by the urban population, culminated in 1950 in the removal of all Federal taxes from margarine. Gradually, state restrictions have been repealed, until today only two states, Wisconsin and Minnesota, prohibit the sale of coloured margarine. A few states, however, do assess taxes against coloured margarine.

This does not mean that margarine manufacturers are totally unregulated. The Standard of Identity as promulgated by the Food and Drug Administration of the Department of Health, Education and Welfare, specifies the required and optional ingredients, and no ingredient not specifically mentioned is permitted. The Food and Drug Administration also has powers of inspection for sanitation as well as the power to prosecute for violation of the Standard of Identity.

III. Major Ingredients

A. Fats

By law, in the United States, 80 per cent of the finished margarine must be fat. Broadly speaking, any edible fat with the proper consistency can be used to make margarine. However, economic factors and such problems as flavour reversion limit the field to a relatively few fats and oils which need be considered from the practical point of view.

There are certain requirements for a suitable margarine fat which are far more critical than those for any other fat product. The reason for this is that, unlike cooking fats, margarine is taken into the mouth often in the unmelted state in relatively gross amounts. In addition to flavour, the feel of the fat in the mouth, the quickness with which it melts, and whether or not it leaves an unmelted residue are all important in the enjoyment of eating margarine.

1. *Flavour*

The flavour of a suitable margarine oil must be completely bland in order not to interfere with the butter-like flavour developed by the milk. Moreover, it

is important that this neutral flavour be maintained throughout the shelf-life of the product, and any oil with a tendency to revert in flavour is undesirable.

2. *Consistency*

Consistency is equal in importance to flavour in margarine. 'Consistency' covers all the physical characteristics, such as spreadability, printability, stand-up properties, and meltdown properties.

The ideal margarine oil must be easily spread at a temperature of 45°F (7°C); but because it must be printed and packaged at about 60°F (15–16°C), the product should be as firm as possible. Also, for those retail outlets which do not display and store margarine under refrigeration, it should not lose its shape or leak oil at 80–86°F (26·7–30·0°C). On the other hand, the margarine should melt quickly and cleanly in the mouth and leave no unmelted material to coat the palate, with the resulting unpleasant sensation which is often referred to as 'pastiness' or 'gumminess'.

With the widespread use in the United States of mixtures of cottonseed and soybean oils, it has been the common practice to hydrogenate these oils, either separately or blended, under the most selective conditions, to give a maximum build-up of *iso*oleic acids and a minimum of stearic acid. This gives a fat with a firm body at processing temperature and a sharp melt-down in the mouth. However, it does suffer the disadvantage of being hard and difficult to spread at refrigerator temperature.

By skillful blending of two or more components hydrogenated to different degrees of hardness, a blend can be made which is significantly softer at 40–50°F (4·4–10·0°C), is about the same degree of hardness at room temperature, and has slightly better stand-up properties. This blend is very popular with the American consumer, where mechanical refrigeration in the home is almost universal, and where it is the custom to keep the margarine in the refrigerator except when it is actually being used.

Typical of the difference between the non-spreadable and spreadable oils is the comparison at several temperatures of the solids content; i.e. the percentage of solid glycerides existing in the oil at a given temperature.

Temperature			
°F	°C	Spreadable	Non-spreadable
50	10·0	31·3%	40·8%
60	15·6	25·5%	33·1%
70	21·1	18·5%	23·0%
80	26·7	13·7%	15·2%
92	33·3	4·5%	2·4%

It is apparent that the difference of almost 10 per cent in the solids at the lower temperature would make the margarine considerably softer at this temperature. At 60°F (15·6°C), or printing temperature, there is still somewhat less solids than

in the non-spreadable type, and this makes the spreadable oil more difficult to print on automatic equipment. However, by close control over temperature, the product can be processed without significant loss of efficiency. The percentage of solids at 92°F (33·3°C) is considerably higher in the spreadable type of oil. This contributes to its stand-up properties, but does not contribute materially to the 'gumminess' or 'pastiness' of the product. According to STRUBLE (1954), in the long plastic-range fats the melting point can be somewhat higher than body temperature if the solids content at that temperature is not more than 2½ per cent; with a sharp-melting fat the melting point should be several degrees lower. The reason for this lies mostly in the slope of the solids content–temperature curve in the region near the melting point. For a wide plastic range fat the slope will be relatively flat, and the solids content curve can extend somewhat beyond body temperature even though the solids content at that temperature is relatively low. For a sharp-melting fat the slope will be relatively steep, and therefore the opposite result will occur.

The dilatometer test is used to control the hydrogenation and blending of these spreadable oils, for the percentage of solids throughout the plastic range is highly important to ensure the desired characteristics of spreadability, printability and melt-down. Most of the dilatometer tests are of the simplified variety, and results are reproducible but largely empirical. A useful simplified method for determining the 'solids content index' is described by FULTON *et al.*, (1954).

3. *Keeping quality*

Just as it is important that a margarine oil should not revert, it is equally important that it should not develop oxidized or rancid flavours during normal shelf-life. In the United States method of distribution margarine normally reaches the ultimate consumer in 1–12 weeks, and this might be considered normal shelf-life. However, in order to take care of contingencies, the margarine should exhibit no evidence of oxidative rancidity under reasonable storage conditions (not over 60°F (15·6°C) after 6 months. With modern refining techniques, most margarine oils properly handled can easily meet this requirement.

As with any fat product, the sooner a margarine oil is made into finished goods after it leaves the deodorizer, the better. However, this is not always possible, because often the oil is transported hundreds of miles from the refinery to the margarine plant. In this case, precautions to avoid overheating and exposure to the air must be taken during the re-melting and transferance from tank car to plant storage tank. A good index as to the future keeping quality of the margarine is a test for peroxides (LEA, 1939) after the oil has been re-melted. If the peroxide value is still quite low, there is reasonable assurance that the margarine will have good keeping quality. If there is a significant amount of peroxide present, there is every reason to assume that the peroxide value will continue to increase rapidly, and the margarine will become rancid in a short time.

B. Animal fats

In the days before the deodorization of vegetable fats was developed, the only fats bland enough in flavour for use in margarine were oleo oil and neutral lard.

1. *Oleo oil*

This is the softer portion of beef fat which is obtained by fractional crystallization at 85–90°F (29·4–32·2°C). It resembles butterfat in physical characteristics, being firm at low temperature and easily melting in the mouth. Oleo oil was the original margarine fat, and it continued to have a predominant role for many years.

2. *Neutral lard*

Neutral lard, produced by the low-temperature wet-rendering of pork fat, was later used in conjunction with oleo oil.

3. *Oleo stearine*

The harder portion remaining from the fractional crystallization of beef fat to produce oleo oil is the classic natural hardener. After the advent of the vegetable oils, oleo stearine was used to raise the melting point of the softer oils. Today oleo stearine is still commonly used in combination with liquid cottonseed oil for Danish roll-in and puff-paste margarines.

Although the consistency of oleo oil–neutral lard mixtures was very good for margarine, there were some drawbacks. In order to obtain a flavour suitable for margarine, rendering had to be carefully done and only the freshest fat used. In addition, these fats are very susceptible to oxidation and the development of off-flavours.

With the improvement in refining and deodorization techniques, vegetable oils began to come to the forefront, and at present only an extremely small percentage of margarine is made from animal fat.

C. Vegetable oils

1. *Coconut oil*

This was the first vegetable oil to come into common usage in margarine. This occurred during the World War I years. Coconut oil alone had too low a melting point, but the addition of oleo stearine and later, hydrogenated coconut oil raised the melting point. Coconut oil margarines were very brittle at low temperature, and often a liquid oil, as well as a harder oil, was added to improve plasticity.

Although coconut oil was by far the most prominent of the group, similar oils such as *palm kernel oil* and *babassu oil* were used to some extent.

In spite of its brittleness at low temperature, a coconut oil margarine has a sharp, clean 'break' in the mouth which resembles butter, and which cannot be duplicated with the hydrogenated oils. Also, coconut oil can be deodorized to the bland flavour desired by the margarine manufacturer, and it is quite resistant to oxidation. It is small wonder, then, that coconut oil rose rapidly in

popularity until by 1929 it was the predominant oil used by the industry, constituting more than 60 per cent of the total fats used in margarine.

In the early 1930s during the great depression, it became politically unpopular as well as uneconomical to use coconut oil in margarine in the United States, and its use rapidly diminished until now little or no coconut oil margarine is made.

In Canada, where there is no prejudice against coconut oil, it is used to some extent in mixtures with cottonseed and soybean oil, and coconut oil is a common ingredient of margarine blends in Europe.

2. *Cottonseed oil*

Cottonseed oil is a by-product of the basic crop of the southern United States. Since the advent of commercial hydrogenation it had been used in shortening but it was not thought possible to produce a margarine oil of suitable characteristics by hydrogenation. Therefore the role of cottonseed oil in margarine had been the minor one of a liquid oil.

The tremendous surplus of this domestic oil and the political unpopularity of foreign coconut oil in the 1930s stimulated refiners to improve their techniques of hydrogenation to the point that they were able to make a product with a much better plastic range than the coconut margarine.

3. *Soybean oil*

This did not become commercially significant in the United States until the 1930s. The oil produced at that time had a characteristic 'beany' odour and flavour, and with a tendency to 'revert' or to re-develop the beany flavour after deodorization. Consequently soybean oil was used with extreme caution by margarine manufacturers. Through the years, by selection of varieties and by improvements in methods of extraction, refining and hydrogenation, the quality of soybean oil has been improved amazingly, so that today the finest quality margarines made in the United States may contain up to 60 per cent or more soybean oil.

4. *Peanut (or groundnut) oil*

This is not largely used in the United States. It is a perfectly acceptable oil, but comparatively little of it is produced, and the majority of it is used as a liquid cooking oil. Peanut oil, however, is used extensively in the United Kingdom and Europe.

5. *Palm oil*

Palm oil suffers the same disadvantages as does coconut oil in the United States. Palm oil also suffers the disadvantage of being highly coloured and extremely difficult to bleach to a colour acceptable to a trade accustomed to the lighter-coloured oils. However, some palm oil is being used in conjunction with other oils in Canada and Europe.

6. *Sesame oil*

Sesame oil is not used in the United States, because of its high price, although it is highly desirable for its keeping quality and bland flavour. A small quantity (5–10 per cent) is required by law in some European countries, because of its easy identification.

D. Marine and marine animal oils

The fish oils, pilchard, sardine, menhaden, etc., are not used in the United States for margarine. Some fish oil is being used to a small extent in Canada.

Whale oil is the most important source of margarine oil in Europe, although it is not used in the United States and Canada.

In Europe, it is the custom to blend four or five or more different kinds of oil of different degrees of hardness together. This may be due largely to the availability of more kinds of oil. It is also believed by some that a multi-component blend gives an oil with better physical characteristics.

In the United States, as mentioned, soybean and cottonseed oils overwhelmingly predominate. This condition has existed for about 20 years, and there is no immediate prospect that it will change. However, recently, great advances have been made in the use of lard and mixtures of lard and vegetable oils in shortening. By hydrogenation and molecular rearrangement, the molecular structure of lard has been modified to approach the more random distribution found in hydrogenated vegetable oils, and this has resulted in a crystal structure which behaves very much like a hydrogenated vegetable oil. The addition of antioxidants like NDGA (Nordihydroguaiaretic Acid), BHA (Butylatedhydroxyanisole), and propyl gallate has increased the ordinarily poor keeping quality of lard until it is comparable to the best vegetable shortenings. It is not inconceivable that improvements of this sort might make lard once again a popular ingredient of margarine oil.

E. Milk

Fat, by virtue of its comprising 80 per cent of the margarine and determining its physical properties, is its most important ingredient. Milk, which comprises 16 per cent or more of the margarine contributes the flavour. Qualitatively, if not quantitatively, it is equally as important to the finished product as the oil.

Mège-Mouriés thought he was producing a butter-like flavour in his margarine by digesting it with macerated cow's udder. No doubt what actually took place was a spontaneous souring of the milk by bacterial action, which produced a butter-like flavour. Not long after, it was observed that a more butter-like flavour could be produced by souring the milk before incorporating it with the fat, and the use of cows' udders was discontinued.

At first, spontaneous souring of milk was practised. Later, the use of 'starters' was established. A 'starter' was a small percentage of a previously soured milk added to a fresh lot of milk to start its fermentation.

With the use of 'starters' it became apparent, both in butter making and in margarine manufacture, that certain starters produced a more pronounced butter-like flavour and aroma than others. This was then narrowed down to the

fact that certain strains of bacteria produced this superior flavour and aroma. From this developed the practice of growing pure cultures and using only those which give the desired characteristics to the cultured milk. Today, practically all cream for butter and skim milk for margarine which is soured is fermented with selected butter cultures.

Bird and Nielson, in another chapter in this volume have discussed the chemistry and propagation of milk cultures in connection with butter making. All that is said about the culture of cream for butter applies equally to the culture of skim milk for margarine manufacture; the organisms involved are the same, and the goal of a richly flavoured culture is the same in either case.

Until recently, it was the practice of nearly all margarine manufacturers in the United States to culture all the milk used in the margarine. About 10 years ago, along with the trend toward milder flavours in all foods, there was a shift toward using mixtures of cultured and sweet milk to produce a milder flavour and to make a margarine more nearly resembling sweet cream butter.

Today, very little margarine in the United States is made with all cultured milk. Several popular brands use mixtures of half cultured milk and half sweet milk; others use little or no cultured milk and depend on the addition of diacetyl for the flavour.

There is no question that the use of all cultured milk gives a distinctly flavoured margarine, resembling the flavour of butter made from sour cream. In certain sections of the United States, particularly in the south, this flavour is popular because it is associated with the butter which they have always had. In other parts of the country, where sweet cream butter, or more mild-flavoured butter is available, the popular taste is for a milder flavour, and the margarines made with smaller amounts of cultured milk are more popular.

The margarines made with sweet milk and diacetyl have a 'cleaner' flavour which is more uniform. Those which depend on a mixture of cultured milk and sweet milk have more overtones of flavour, but since it is dependent on natural processes, there is likely to be more variation in flavour from one day to the next, and less certainty as to the stability of the flavour as the margarine ages.

1. *Quality of milk*

Whether a skim milk is to be used unsoured or is to be cultured, only the best quality should be considered for use in margarine. The milk should have good body; i.e. the specific gravity should be at least 1·034 (60°F), to insure sufficient non-fat solids to make it nutritionally acceptable. Needless to say, it should be sweet and clean in flavour and free from pasturage or barny flavours. It must be free of all filth and reasonably free of other sediment.

The milk may be received at the margarine plant either unpasteurized or flash-pasteurized; in either case it is the custom of the margarine manufacturer to re-pasteurize it. Pasteurization at a higher temperature is not as injurious to the flavour of milk for margarine as it is for milk designed for drinking, so it is the common practice to pasteurize at temperatures of 180–190°F (82–88°C), to

be sure that all dangerous bacteria are destroyed. Pasteurization is commonly carried in steam-jacketed tanks fitted with slow-speed sweep agitators. The milk is brought up to pasteurizing temperature as quickly as possible, and cooled by introducing cold water in the jacket. If the milk is to be cultured, it is brought to 70°F (21°C) and inoculated with 2–2·5 per cent starter, then the agitation is stopped, and the temperature held at 70°F (21°C) for 12–16 h. If the milk is to be used sweet, it is cooled as much as possible and used the same day.

The acidity, calculated as lactic acid, on the milk as received at the plant ranges from about 0·12 to 0·17 per cent. If the acidity is much above 0·20 per cent even though the flavour is sweet, it is risky to use the milk, for it is likely to curdle on pasteurization.

2. *Non-fat dry milk solids*

While the use of fluid skim milk is convenient where an adequate supply of good quality is available, there are many parts of the world where such a supply is not available. In such cases, reconstituted spray-dried skim milk is a satisfactory substitute. Spray-dried skim milk, or 'non-fat dry milk solids' as it is commonly designated, is in the form of a light cream-coloured powder. The moisture is less than 4 per cent and the material keeps well without refrigeration. Packaging is in fibre drums, or more recently in paper bags with a polyethylene liner.

Non-fat dry milk solids are commonly bought in the United States on specifications established by the American Dry Milk Institute (1944).

3. *General requirements for all grades*

All non-fat dry milk solids for human consumption shall conform in all respects to Federal and State government regulations in force at the present time or that may be subsequently issued from time to time.

The factory and factory equipment used in the manufacture of non-fat dry milk solids shall be maintained in a strictly clean, sanitary condition. No person or persons affected with any infectious, contagious, or communicable disease, or who resides, boards or lodges in a household in which there is a person affected with such disease, shall be employed or permitted to work in or about any part of the factory in which non-fat dry milk solids is manufactured.

Non-fat dry milk solids shall be made from fresh, sweet milk to which no preservative, alkali, neutralizing agent, or other chemical has been added and which has been pasteurized in the liquid state either before or during the process of manufacture at a temperature of 143°F for 30 min or its equivalent in bacterial destruction.

Non-fat dry milk solids shall be reasonably uniform in composition. The colour shall be white or light cream and free from a brown or yellow colour typical of overheated stock and free from any other unnatural colour. It shall be substantially free from brown specks.

The flavour and odour of non-fat dry milk solids in dry form or on reconstitution shall be sweet and clean and entirely free from rancid tallowy, fishy, cheesy, soapy, or other equally objectionable flavours or odours.

Non-fat dry milk solids shall be packed in substantial containers which have been tested and approved by the American Dry Milk Institute as suitable to protect and preserve the contents without significant impairment of quality with respect to sanitation, contamination and moisture content under various customary conditions of handling, transportation and storage.

4. *Specific requirements for extra grade*

Extra Grade is so designated to indicate the highest quality of non-fat dry milk solids and, in addition to the foregoing General Requirements, must meet the following specifications:

	Spray *Not greater than*	*Vacuum drum* *Not greater than*	*Atmospheric roller* *Not greater than*
Butterfat	1·25%	1·25%	1·25%
Moisture	4·00%	4·00%	4·00%
Titratable acidity (reconstituted basis)	0·15%	0·15%	0·15%
Solubility index	1·25 ml	2·00 ml	15·00 ml
Bacterial count (reconstituted basis	15,000 per ml	15,000 per ml	15,000 per ml
Sediment	Disc No. 3	Disc No. 3	Disc No. 3

In addition, there is a Standard Grade with somewhat lower requirements, but this is not recommended for margarine.

5. *Other drying processes*

Vacuum drum or atmospheric roller drying does not produce a milk suitable for margarine manufacture, chiefly because the solubility index is too high. It is desirable to have as nearly complete solubility as possible, for an accumulation of insolubles in processing equipment, fouls strainers and generally adds to processing problems. In fact, it is the custom of some margarine manufacturers to specify a solubility index of not more than 0·25 ml instead of the ADMI allowance of 1·25 ml. Solubility indices of 0·10 ml or less are commonly found in a good quality of dried milk.

6. *Reconstitution*

The Standard of Identity specifies that on reconstituting, 'any combination of non-fat dry milk solids and water, in which the weight of the non-fat dry milk solids is not less than 10 per cent of the weight of the water,' may be used. Reconstituted on this basis, the mixture has about the same solids content as fresh skim milk, and when used unsoured is indistinguishable from fluid milk in the finished margarine. In making cultured milk, however, reconstituted non-fat

dry milk has a tendency to form a weak, watery curd and to be somewhat flat in flavour. A great deal of improvement in this, however, has been made by the fairly recent introduction of so-called 'low-heat non-fat dry milk solids'. As indicated by the name, this is made by spray-drying the milk at a lower temperature than is normally used. This 'low-heat' powder makes a much better cultured milk, and it might be said that it is almost equal to fluid skim.

Reconstituted powdered milk is always pasteurized in the same manner as fluid milk before use.

In the revised Standard of Identity, effective in August 1952, on the petition of a group who wished for a spread resembling butter but not containing any animal product, a product in which the skim milk is replaced by a suspension of finely ground soybeans and water in which the weight of the finely ground soybeans is not less than 10 per cent of the weight of the water was permitted. Previously, such a product could not be sold because although it was margarine by statutory definition, it did not comply with the Standard of Identity for margarine.

IV. Minor Constituents

A. Salt

Salt has two important functions in margarine. One is as a preservative, to protect the milk portion from bacterial growth. Of more importance is its function in flavour. Salt is noted in all foods for its ability to bring out and point up flavour. This is particularly true in margarine. Even though the other flavour ingredients may be exactly the same as in a good salted margarine, an unsalted margarine is flat and tasteless.

Geography plays an important part in the popular taste for salted foods. European margarines, as well as European butters, contain considerably less salt than American margarines, usually 1·0–1·5 per cent. In the United States, most margarines average about 3·0 per cent. The eastern United States usually prefers less salt, and the south and south-west like a high salt content.

Since the salt is dissolved in the aqueous phase of the margarine, the fineness of the dispersion of the milk phase in the fat has a distinct bearing on the salty taste. A fine dispersion of the milk tastes less salty than a coarse dispersion.

For margarine, a salt of high purity is preferred. It should be low in calcium and magnesium, and copper should be less than 1 p.p.m. Above all, the salt should dissolve quickly and completely in the milk. Because of its rapid dissolving quality, flake butter salt is commonly used, although certain purified grades of granulated salt are satisfactory.

B. Lecithin

A natural property of butter is that of foaming and boiling off the moisture without spattering when placed in a frying pan. In addition, when the moisture is driven off, the curd browns without sticking to the pan and imparts to food fried in it a particular flavour. Without the use of a surface-active agent, when margarine melts, the aqueous portion settles rapidly to the bottom. Steam generated

under the surface of the oil tends to erupt suddenly, causing violent spattering. Also the milk curd settles and tends to burn and adhere to the pan.

Probably the first material to gain popularity as an additive to margarine to prevent spattering was egg yolk. In May 1884 a German patent was issued to HEISSBAUER, covering the use of egg yolk in margarine. The use of egg yolk continued in many European countries for some time, although apparently it never achieved any popularity in the United States.

With the development of methods for extracting vegetable lecithins, particularly soybean lecithin, from the crude oils, these lecithins are now commonly used as anti-spattering agents both in Europe and the United States.

Lecithin, in very small percentages, is a powerful surface-active agent, lowering the interfacial tension between the oil and water. By this lowering of interfacial tension, the steam generated by heating boils quietly out with foaming rather than spattering, and the curd browns without adhering.

Commercial lecithin is far from a simple compound. P. DESNUELLE (1952) has dealt extensively with the structure and chemistry of the phospholipids. It is not necessary here to go into the chemistry or preparation of commercial lecithin, since this is covered by Cowan in another chapter in this volume.

Soybean lecithin is by far the most commonly used commercial lecithin, although a small amount of corn oil lecithin has been used in margarine manufacture.

Aside from its ability to suppress spattering and to cause browning, an acceptable commercial lecithin must have a viscosity low enough to mix readily with oil. It is commonly mixed with an equal amount of liquid oil further to reduce the viscosity so that it will be readily dispersible in the larger volume of margarine oil. It should also be stable in flavour. Even though it is used in quantities of less than 0·5 per cent some lecithins will revert in flavour and contribute a 'beany' or fishy flavour to the margarine on ageing. Although the colour is of relative unimportance, it is thought by some margarine manufacturers that bleached lecithins are somewhat more stable in flavour and slightly more effective functionally.

Lecithin is used in various percentages, from 0·10 to 0·50 per cent depending on the margarine manufacturer. The Standard of Identity prohibits the use of more than 0·50 per cent.

C. Monoglycerides and diglycerides

Margarine with no emulsifying agent has a tendency to 'weep' or ooze moisture during storage. If a very fine dispersion of the aqueous phase in the oil is made, there is less tendency toward this leakage, and lecithin is fairly effective. However, lecithin is much less effective than monoglycerides and diglycerides, and these materials are commonly employed in combination with the lecithin. The monoglycerides and diglycerides have an ability to imbibe or 'bind' large quantities of water. In this respect the monostearates are considerably more effective than the softer monoglycerides and diglycerides. In concentrations of 0·20–0·50 per cent monostearates and distearates effectively prevent 'weeping'.

Bailey (1951a) has described in detail the manufacture of monoglycerides and diglycerides.

1. *Distilled monoglycerides*

The monoglyceride portion is considered most effective and the highest possible percentage of monoglycrides is considered desirable.

Recently, there has become available a material containing 90–95 per cent pure monoglyceride, obtained by molecular distillation of the mixed glycerides. These distilled monoglycerides are more expensive, but it is claimed that they are more economical because they are effective in much less quantity than the mixed glycerides.

2. *Sodium sulpho-acetate derivatives*

The monoglycerides are not effective 'anti-spattering' agents, but their sodium sulpho-acetate derivatives are quite effective, and they are used by some margarine manufacturers as both 'anti-spattering' and anti-weeping' agents.

D. Sodium benzoate and benzoic acid

Sodium benzoate or benzoic acid, to the extent of 0·10 per cent are the only preservatives permitted in margarine by the U.S. Standard of Identity. Benzoic acid, because of its limited solubility, is not popular, and sodium benzoate is commonly used. Sodium benzoate is available in either powder or flake form. The flake form is more easily soluble and is usually preferred.

The chief function of benzoate is to protect margarine from mould growth, to which it is susceptible because of the presence of moisture and milk solids. The trend toward lower acidity in the milk used in margarine has considerably diminished the effectiveness of sodium benzoate as a mould inhibitor. It is an established fact that sodium benzoate is most effective in an acid medium, and that the effectiveness decreases with increase in pH. As less cultured milk has been used in margarine, the pH has increased from about 4·0–4·5 to 6·0–6·5. Although there is some protection afforded by benzoate even at these high pH values, its protective value has been reduced. On the other hand, improved sanitary procedures, a closed processing system, and improved protective packaging materials have substantially lessened the danger of mould contamination and thus have made the use of sodium benzoate less necessary.

Even though sodium benzoate has been used for many years with the full approval of the Federal Food and Drug Administration, and in spite of the demonstrated fact that it is completely harmless, there is a certain prejudice by some people against the use of any preservative in any food. This prejudice apparently is not wide-spread, but it crops up occasionally in local legislative restrictions.

E. Vitamins

As soon as the importance of the vitamins in the diet was discovered, it became apparent that butter was a fairly rich source of the fat-soluble vitamin A, and to

a lesser extent, a source of vitamin D. The fats commonly used in making margarine are lacking in these vitamins, so methods were sought to fortify margarine with these vitamins in order to bring margarine nutritionally equal to butter.

1. *Vitamin A*

The amount of vitamin A in butter varies greatly with the seasons and the diet of the cow. Spring and summer butter is rich in vitamin A because the animals are feeding on green pasturage. Winter butter is quite low in vitamin A. Butter ranges from about 5,000 USP units/lb in winter, to as high as 20,000 units/lb in spring and summer.

Probably the first attempts at fortification of margarine with vitamin A were to add fish-liver oils, known to be rich in the vitamin. While the fish-liver oils are relatively vitamin rich, their potent odour and flavour would prohibit their addition in amounts that would afford a substantial fortification of the margarine.

Later, methods were found to concentrate the vitamin and greatly alleviate the odour problem. Improved techniques resulted in concentrates of 300,000 to 400,000 units/g. At best, these concentrates possessed a strong fishy odour and flavour. Their virtue was that only a small amount was required, and, in general no flavour was transmitted to the margarine. There have been cases however, when even these high potencies reverted in the margarine and produced an unpleasant fishy flavour.

(a) *Synthetic vitamin A.* The successful commercial synthesis of vitamin A opened up a new source free of the objectionable flavour and odour. Synthetic vitamin A was used in pharmaceuticals for some time before its use in margarine was permitted. The original Standard of Identity, promulgated in 1941, specified only fish-liver oil or a concentrate from fish-liver oil, since these were the only common sources of the vitamin available. It was necessary to amend the Standard of Identity to permit the use of synthetic vitamin A. This was done in 1952, and since then practically every major margarine manufacturer has switched to the synthetic. This switch has been materially aided by the low and stable price of the synthetic. Natural vitamin A was subject to wide fluctuations in price, depending on the ability of fishing fleets to supply the demand. Synthetic vitamin A is not subject to such fluctuations in raw material, and as usage has increased, production economies have resulted in steadily decreasing prices.

A valuable service to the margarine manufacturer which the vitamin suppliers have offered for the past few years is the packaging of the vitamin in hermetically sealed, batch-size cans. These cans are custom-packed for each manufacturer. Each can contains the exact number of units of vitamin A required for a batch of the manufacturer's margarine. The cans are usually of uniform size, containing about 400 g net. The actual amount of concentrate varies, depending on the requirements of the individual manufacturer, but the concentrate is diluted with cottonseed or corn oil to 400 g. These cans are packed in an inert

atmosphere of nitrogen, and under these conditions, even without refrigeration, the vitamin A is remarkably stable.

If margarine is fortified with vitamin A, the minimum potency permitted by the Standard of Identity is 15,000 USP units /lb. In the past, when concentrates were not so pure, it was customary to add a 20 per cent excess of vitamin A to protect the label claim. This was based on studies which indicated a loss of about 20 per cent of vitamin A under average storage conditions. Later experience with improved concentrates and synthetic vitamin A has shown that normally there is little or no loss of vitamin A in margarine, and currently most margarine manufacturers are using smaller excesses of 10 per cent or less.

(b) *Assay.* The question of the assay of vitamin A in margarine has always been a difficult one. Concentrates are bought on USP XIV assays. The USP XIV is a spectro-photometric method, employing the Morton–Stubbs correction. It is official for all assays on concentrates. The USP XIV method, however, is not suitable for low-potency material such as margarine. Legally, in the United States, the official method of vitamin A assay in margarine is the rat bioassay. This method is slow, expensive, and lacks precision, so that it is used only occasionally as a check method. For control in the plant, where a blank containing all the materials of the margarine except the vitamin A is available, a direct spectro-photometric assay can be made by comparing the absorption at 328 mμ of a sample of the margarine containing the vitamin A with the blank. This method is not applicable unless a blank containing the same oil and other ingredients as the sample is available, for the absorption of different lots of oil varies greatly. Where a blank is not available, the Carr-Price antimony trichloride method is usually used (Association of Vitamin Chemists, 1947).

2. *Vitamin* D

The addition of vitamin D is fairly common in European margarine, but in the United States its use has been variable. Butter contains 200–500 units of vitamin D per lb, and is not considered a naturally rich source of vitamin D. Various organizations concerned with nutrition do not approve of advocating butter or margarine as a source of vitamin D, and instead have encouraged the fortification of whole milk as the natural carrier of vitamin D.

Those margarine manufacturers who add vitamin D with the idea of making margarine nutritionally equal or superior in all respects to butter usually fortify to a potency of 2,000 USP units/lb.

3. *Vitamin E*

Vitamin E, or the tocopherols, is a recognized vitamin, although its complete role in the body is not thoroughly understood.

Vegetable oils, particularly cottonseed oil, are rich sources of α-tocopherol, while animal fats are extremely poor in the vitamin, which explains why the keeping quality of vegetable oils is much better than that of animal fats.

Margarine made from vegetable oils is an exceptionally fine source of this vitamin. HICKMAN (1948) reports that margarine contains 28·0 mg of α-tocopherol per 100 g, compared with 2·4 mg/100 g for butter.

This great superiority of margarine over butter in vitamin E has never been exploited by the margarine manufacturers. Probably the principal reason for this is that the requirement of vitamin E in the human dietary has not been established.

F. Artificial colours

The matter of colour in butter and margarine varies geographically as much as the taste for salt. European butter and margarines are quite light in colour, almost white. This may have its origin in the diet of the cows, where a deficiency of green pasturage causes the cattle to be fed largely on oil cake and other protein feeds. The butter from these cows would be light in colour, and once a national acceptance for this shade of butter was established, margarine naturally would follow.

In the United States, however, the people developed a liking for the highly coloured spring butter, when the cattle were feeding on ample green pasturage. In 1886, Congress permitted the artificial colouring of butter, and it became the custom to colour winter butter artificially to give it the same colour as spring butter. Now all dairy butter as well as margarine is relatively highly coloured. The same artificial colours are used in both butter and margarine, although the varying natural colour of butter causes not so much to be required for butter as for margarine.

1. *Annatto*

The earliest colour commonly used in margarine was annatto. This is a vegetable colour derived from the seeds of *Bixa orellana*, a plant which grows in south and central America and the West Indies. Annatto gives an excellent natural colour to margarine, but it has some definite drawbacks. In the first place, it is more expensive than the aniline dyes, and in addition, it suffers from a lack of uniformity and keeping quality. On storage for a length of time, the colouring power of the material gradually diminishes, and this makes it difficult for the manufacturer to standardize his colour.

Recently, an effort has been made to improve the extraction of the active colour principle from the seeds of *Bixa orellana*. Previously, the annatto extracts were obtained by alkali extraction. The improved extract is obtained by solvent extraction, and is claimed to be stable. The extract contains two fractions. One of these is bixin ($C_{16}H_{26}O_2$), which is crystallized from the solvent and purified. Bixin is a dark, reddish orange pigment, which is very difficultly soluble in vegetable oil. The other fraction, left on evaporation of the solvent, is an amorphous mixture of carotenoid-xanthophyll pigments, which are the yellow pigments.

It is reported that these pigments can be mixed in the proper proportions to give any desired shade of colour. The poor solubility of the bixin, however, has

been the problem, and this has not been completely solved. One manufacturer has offered experimental quantities of this colour in batch-size cans along with vitamin A, which look promising; but this material at present can only be considered in the experimental stage.

2. *Certified food colours.*

In 1908 (INSKEEP and KRETLOW, 1952), after the wide variety of aniline dyes being used in foods was carefully screened for toxicity, the system of certified food colours was established by Food and Drug Administration. The number of dyes originally eligible for certification was optional, and the use of uncertified colours continued to be extensive. From time to time, more dyes were declared eligible for certification, and in 1918 oil-soluble Yellow AB and Yellow OB were approved and were designated FD & C No. 3 and FD & C No. 4 respectively.

The Food, Drug and Cosmetic Act of 1938 specifically prohibited the use of any uncertified colour in any food, drug or cosmetic shipped in inter-state commerce. According to the law, each batch of food colour is tested and certified by Food and Drug Administration. The batch is given a number, and this number must be plainly indicated on each package of dye sold. If the dye is mixed with other materials, the mixture must be re-certified.

Most margarine manufacturers use a mixture of FD & C yellows 3 and 4. The proportion of each is largely a matter of the choice of shade desired by the individual manufacturer. FD & C No. 3, or benzeneazo-β-naphthylamine, contributes more of a pure yellow shade to the margarine. FD & C No. 4, or *o*-tolueneazo-β-naphthylamine, has more of a reddish tint. The majority of margarine manufacturers favour a mixture ranging from equal quantities of each to a greater or less preponderance of No. 4. As to the quantity of dye used, this is also variable depending on the individual manufacturer, but it does not deviate far from the average of 0·0025 per cent pure dye.

Before the tax on coloured margarine was repealed in 1950, most margarine manufactured in the United States was uncoloured. It was then customary to supply with each pound of uncoloured margarine a packet of dry colour which could be worked into the margarine by the consumer. This dry colour consisted of the dye mixed with an inert diluent such as cornstarch, the pure colour amounting to about 15 per cent of the total. In the case of the sealed plastic bag, the colour was dissolved in liquid oil and encased in a gelatin capsule which could be ruptured by pressure of the fingers, releasing the colour which could then be worked into the margarine by kneading the bag.

Now, most margarine in the United States is coloured by the manufacturer. The dye is commonly dissolved in liquid oil, and a measured amount of this solution added to each batch. Some manufacturers buy liquid colour, while others purchase the pure dyes and make their own solutions. The concentration of pure dye in these solutions ranges from 3 to 6 per cent, 6 per cent being practically the upper limit of solubility.

It was mentioned that the suppliers of vitamin A were offering the vitamin in

batch-size cans. Recently the major vitamin suppliers have offered a batch-size can containing, in addition to the vitamin A, the required amount of colour for each batch. This too, of course, is on a custom basis. This is a little more expensive to the margarine manufacturer than mixing his own liquid colour, but it has certain advantages which offset the slight additional cost. For one, it has the same advantage of uniformity and cleanliness as the batchsize vitamin can. Perhaps the most significant advantage, however, is that the dye serves as a marker for the vitamin, assuring that it has been added to the batch. As in any batch process, there is always the possibility that an ingredient may be overlooked by the workman making up the batch. Because vitamin fortification is one of the major label claims of the margarine manufacturer, and because he has a moral as well as legal obligation to see that the vitamin is present in the specified quantity, it has always been one of the chief concerns of the margarine manufacturer that the vitamin is actually in the margarine. With the dye in the sealed can along with the vitamin, there is less possibility that the vitamin can be omitted. This inclusion of the colour in the can with the vitamin is comparatively new, and so far has not gained widespread usage.

3. *Carotene*

Carotene is the material responsible for the natural colour of butter. Therefore, it might be said that it is the ideal colour for margarine as well as butter. This is true, except that commercial carotene preparations have suffered from lack of uniformity, scarcity and high price.

Concentrates of natural carotene have been prepared from a variety of sources, the chief of them being alfalfa, palm oil, and carrots. The alfalfa preparations have usually contained too large a proportion of chlorophyll to make them acceptable as margarine-colouring materials. They have a tendency to give margarine a greenish-yellow cast, and in some cases, a 'green grass' flavour.

Palm oil concentrates are acceptable for margarine colouring, but they are in short supply and high in price.

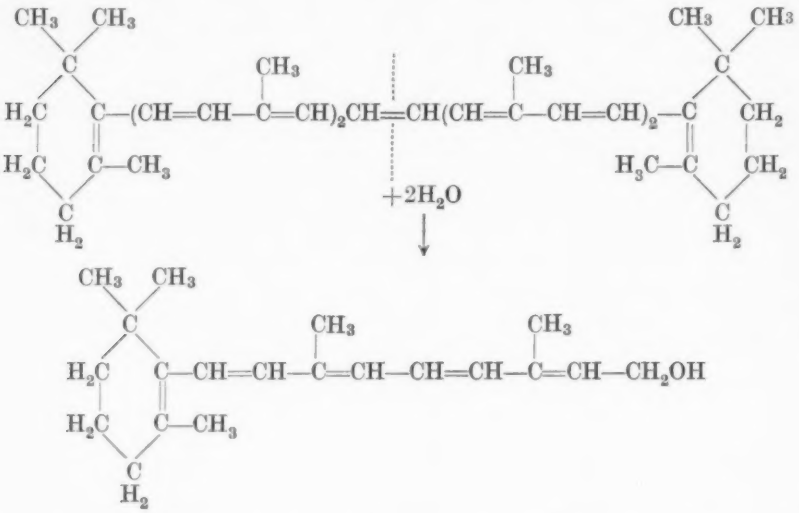
The most plentiful supply of carotene concentrate is derived from carrots. Even then, it is doubtful if existing supplies could accommodate more than 25 per cent of the margarine industry, and the cost is more than double that of the coal-tar dyes. Carotene concentrates from carrots, when properly prepared, are very satisfactory.

The preparation of these concentrates is described by Luckmann *et al.*[14]

Carotene occurs in three isomeric forms. α- and β-carotenes frequently are found together, but the β- form invariably predominates. γ-carotene occurs only in minute percentages. All the carotenes are provitamin A, but β-carotene is twice as active as the others.

β-carotene functions as provitamin A by virtue of its being oxidatively split in the body, apparently in the liver. This is of particular importance, since apparently the higher animals are incapable of synthesizing vitamin A in the body.

This oxidative splitting, with β-carotene furnishing two molecules of vitamin A, is illustrated by the formula (LEA, 1939).



Pure β-carotene is capable of producing 1,666,000 U.S.P. units of vitamin A per g. Since the interest in carotene is based on its vitamin A potency as well as its colouring ability, carotene preparations are usually spoken of in terms of their vitamin A potency rather than in terms of weight.

Even in the United States, where highly coloured margarines are preferred, it is not possible to add the equivalent of more than 5,000–7,000 units of vitamin A per lb as carotene, because the colour would be too dark. The remaining 10,000–8,000 units of vitamin A must be added as vitamin A.

Because carotene furnishes vitamin A as well as colour, it undoubtedly would be the preferred colouring material of all margarine manufacturers if the supply and price could be brought into line. Recently, the synthesis of β-carotene on a commercial scale has been undertaken by at least one vitamin manufacturer. The batch-size can containing carotene for the colouring material and sufficient vitamin A for the desired fortification is now available. Once manufacture on a commercial scale was attained, the price has followed the usual downward trend of most synthetic materials. Therefore, it is quite within the realm of possibility that synthetic carotene will shortly replace all other colouring materials in margarine.

G. Artificial flavours

The roles of diacetyl and acetylmethylcarbinol as they occur in cultured milk have been discussed in another chapter of this volume. With the trend toward milder-flavoured margarine, the amount of cultured milk has been decreased so that in many margarines little or no flavour is obtained from the natural source of cultured milk. Accordingly, it is the custom of many margarine manufacturers

to obtain flavour by the addition of pure diacetyl, or diacetyl in the form of starter distillates.

It is the contention of those who use pure diacetyl alone, that it gives a 'cleaner' more delicate aroma and flavour to the margarine. Used in very dilute quantities (1–2 p.p.m.), diacetyl does impart a fresh, sweet flavour to margarine, as opposed to the more complex (sour cream) flavour imparted by cultured milk. The choice between the flavour of diacetyl alone or the cultured milk flavour is based largely on the opinion of the margarine manufacturer as to which type of flavour his customers like. Of the brands of margarine leading in sales in the United States, about half use diacetyl alone, and the other half use cultured milk for flavour, so it seems that the consuming public has no definite choice as to the type of flavour used.

It has been observed, however, that the margarines using diacetyl only are more uniform in flavour than those with cultured milk. This is only to be expected, for it is rather difficult to meet a production schedule with an exactly uniform product derived from such a complex biological process as the fermentation of milk.

A mixture containing 1 part of diacetyl to 8 parts of acetylmethylcarbinol is offered to United States margarine manufacturers, with the claim that the acetylmethylcarbinol continues to supply diacetyl by oxidation as the diacetyl is dissipated with age. This material, however, has not met with popular acceptance.

For those margarine manufacturers who prefer the more complex flavours of cultured milk without the attendant problems of making cultured milk of doubtful uniformity, there are a number of starter distillates offered. These are concentrates prepared by the steam-distillation of the volatiles from cultured milk. Thus the starter distillates contain the volatile acids which contribute to the flavour of cultured milk, as well as the diacetyl and acetylmethylcarbinol. The starter distillates contain the essence of cultured milk with the added advantage that they can be more easily standardized.

Most of the large flavour houses offer proprietary 'butter flavours' which are more or less complex mixtures of esters and volatile acids. These materials are often advocated for use in margarine, but they are invariably quite expensive if used in the amounts recommended. These 'butter flavours' are largely used by bakers and candy makers and the like to give additional butter flavour to their product.

H. Citric acid and isopropyl *citrates*

Citric acid has long been recognized for the role it plays in promoting the formation of diacetyl in cultured milk. Citric acid is also recognized as a metal-sequestering agent, and when the oil is treated with citric acid in the deodorizer, it is thought by some to increase the keeping quality of the oil by virtue of its ability to remove traces of iron, nickel and other metals dissolved in the oil. It is also thought by some that this treatment with citric acid delays, or possibly prevents, the reversion of soybean oil.

While there is considerable evidence that treatment of the oil by citric acid is of some value, there is still considerable doubt in the minds of some refiners as to its value, and the citric acid treatment of oil is not a universal practice by any means.

Citric acid is only very slightly soluble in vegetable oil, and if it is introduced into the deodorizer, it is largely filtered out at the end of the process. On the theory that if citric acid could be made soluble in the oil so that an appreciable amount could be left in the oil, the beneficial effect could be more extended, patents have been granted (NEAL *et al.*, 1949) on the use of certain esters of citric acid which are considerably more soluble. In the 1952 amendment to the Standard of Identity, the use of *iso*propyl citrate in an amount not to exceed 0·02 per cent by weight of the finished product was permitted. If citric acid is incorporated in the fat, the label must bear the declaration 'citric acid added to protect flavour.' If *iso*propyl citrate is used, the margarine must be labelled, '*Iso*propyl citrate added to protect flavour.'

As in the case of citric acid, the value of *iso*propyl citrate has not been universally established, and at present only one major United States manufacturer is using it.

I. Butter

Since the beginning of margarine manufacture, more or less butter or cream has occasionally been mixed with margarine, usually for its advertising value. Butter, in significant amounts (20–25 per cent) will give to a mild-flavoured margarine a pleasing and somewhat different flavour. However, in these amounts the cost becomes prohibitive, and besides, unless this margarine is kept under excellent refrigeration, it quickly develops an unpleasant flavour. Butter or butterfat in lesser amounts has no noticeable effect on the flavour of the margarine, but it does affect to some extent the keeping quality.

For the double reasons of poor keeping quality and expense, the use of butter or cream is generally avoided by margarine manufacturers.

V. MARGARINE PROCESSING

A. Early methods

The original process of margarine manufacture by Mège-Mouriés provided for the churning of the emulsion of fat and milk to impart a butter-like flavour to the fat, and to some extent texturize the product. However, no provision was made for chilling the emulsion, and as a result Mouriés' emulsion must have been very grainy. Mott (SNODGRASS, 1930b) is credited with the important improvement of preventing graining by quick chilling of the emulsion of fat and milk. According to Mott, the emulsion of fat and sour milk was thoroughly mixed in a churn and the mixture withdrawn through a hole at one end and allowed to fall into a tub of cracked ice. As the oil flowed on the ice it was kept in constant motion until the tub was filled with the solidified margarine, when another tub was put in its place. The solidified oil, after remaining in contact with the ice in the tub for two or three hours, was dumped on an inclined table, where the ice

was permitted to melt and drain off. The mixture was subsequently churned with additional sour milk, worked and salted like churned butter. Mott's process eliminated graininess and produced a product with a texture similar to butter. Later, in 1896, with the perfection of mechanical refrigeration, the use of ice-cold water was adopted. At first a sheet of ice-cold water was used, and later the emulsion was sprayed into a sluice where it met a spray of water which crystallized the fat and washed it down into a truck for draining.

In spite of its drawbacks, this method of chilling persisted and was the most popular method of chilling margarine in the United States until about 1940. Even today, it is still used in some plants for producing special-purpose margarines such as puff paste.

In 1907 SCHOU (1907) patented the process of chilling the emulsion by running it over a brine-cooled revolving drum. The use of a chilled drum was not new in the quick chilling of lard and lard compounds but it had not previously been applied to margarine.

The chill-roll process had the advantage of solidifying the emulsion out of contact with the cooling medium, and became quite popular, particularly in Holland and the Scandinavian countries. The chill-roll method was less popular in the United States than the water chilling method, but in some quarters it persisted until comparatively recently, and it is still used to a considerable extent in Europe.

Whether the emulsion is solidified by the water crystallization method or the chill roll, the solidified material appears as a mass of crystals or plates which do not adhere together. In order to produce a smooth homogeneous mass the crystals must be kneaded or worked until they join together and become homogeneous. In the case of the water-chilled product, excess water, amounting to as much as 10–15 per cent of the total must be worked out. Also, salt is usually worked in at this stage. Various forms of workers were used. One of the most common consisted of a flat, revolving round table with wooden rollers tangential to the table surface. The crystals were put on this table and it was revolved until the product reached the desired condition.

Other workers consisted of methods of forcing the chilled emulsion through a series of perforated plates, usually with revolving knives between the plates, so that passage through the plates kneaded the margarine to the desired consistency. Later a blender was introduced, consisting of a box-type holder, equipped with double horizontal agitators. The margarine was loaded into it, a cover placed on it, and the load agitated rapidly for a few minutes. This method insured regular and uniform distribution of the salt, permitted additional milk to be added if desired, and tended to give the margarine a more plastic, less brittle consistency.

The water-crystallization method was inefficient in refrigeration—it required that large amounts of water be chilled to about 36°F (2°C) and be discharged to the sewer at 45°F (7°C). Also, the contact of the water with the margarine presented a serious problem if the water should become contaminated with organisms or a chemical which would be deleterious to the quality of the margarine.

The chill-roll was more efficient in refrigeration, and the product did not come in contact with the refrigerant; but the margarine was exposed to airborne contamination while it was on the roll. With either the roll or the water chilling method, the subsequent handling and working were costly in labour and offered opportunity for contamination of the product.

What was eminently desired was a continuous, closed system method of chilling and working the product under conditions of maximum sanitation and efficiency.

B. The Votator system

In 1936 the answer to this need for a closed continuous system came in the form of the Votator (Fig. 1). Detailed descriptions of all these various methods of solidifying margarine have been given by SLAUGHTER and MCMICHAEL (1949), BAILEY (1951b) and JAMES (1948). JOYNER (1953) has also discussed the various aspects of crystal structure on the consistency and appearance of margarine, as well as giving a detailed description of the votator continuous system.

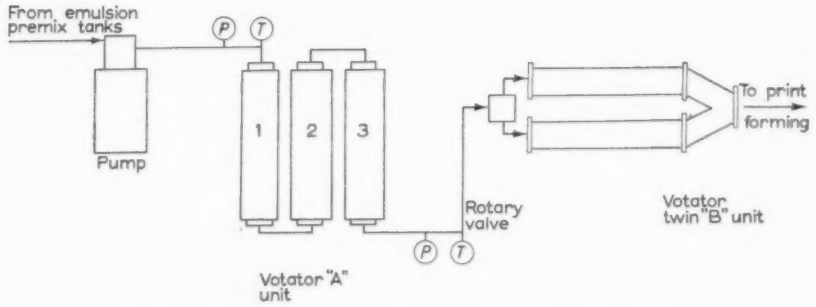


Fig. 3. Flow diagram for the Votator margarine process.
(Courtesy of The Girdler Company, Louisville, Kentucky.)

Essentially the apparatus consists of a scraped-surface heat exchanger (Fig. 2), jacketed for a direct expansion refrigerant system, and an unrefrigerated unagitated tempering zone where the margarine crystallizes and 'sets' with the minimum of working (see Fig. 3 for complete system). The chilling, or 'A' unit consists usually of three horizontal tubes, in series, although single-tube units of lesser capacity are available. The heat transfer tubes are 4 in. (10 cm) in diameter, constructed of commercially pure nickel, chrome plated to minimize cylinder wear and prolong the life of the scraper blades; all other parts coming into contact with the product are of stainless steel. The shafts are $3\frac{1}{4}$ in. (8·25 cm) in diameter, leaving an annular space of $\frac{3}{8}$ in. (0·95 cm). In this space, scraper blades attached loosely to the shaft ride against the cylinder wall by centrifugal force and the viscosity of the material. These blades continuously and rapidly scrape the chilled product from the cylinder wall, presenting a new refrigerated surface to oncoming product. At the same time, the action of these blades provides the violent agitation so necessary to the formation of a fine and uniform crystal structure. In the three-tube system, the emulsion is pumped

Fig. 1. The Votator continuous process for margarine manufacture. (Courtesy of The Girdler Company, Louisville, Kentucky.)

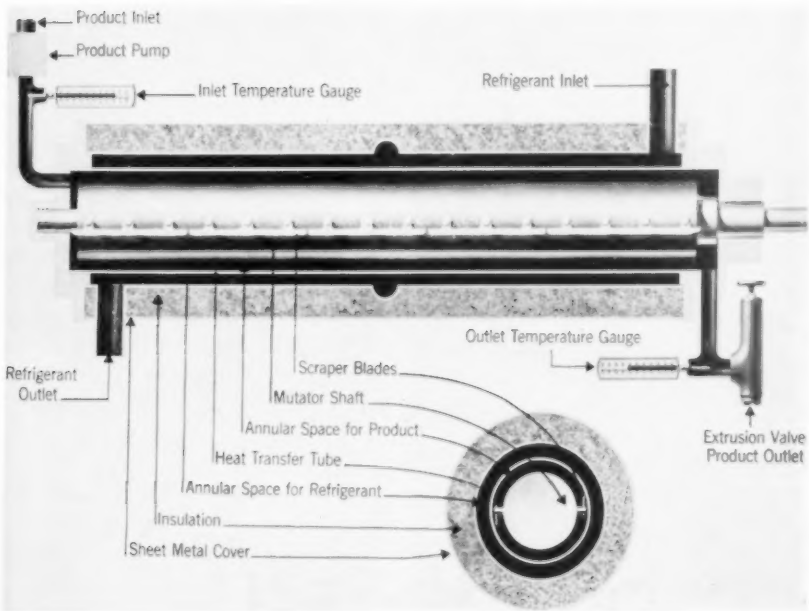


Fig. 2. Longitudinal and cross-sectional view of the Votator heat exchanger for chilling edible fats. (Courtesy of The Girdler Company, Louisville, Kentucky.)

(*To face page 310*)

through the first tube, where it loses some of its heat, then through the second and third tubes, where it is rapidly supercooled below its congealing temperature, although very little crystallization takes place.

In the case of shortening fats, the supercooled fat then goes to an agitated crystallizing or 'B' unit, where crystallization takes place under agitation, to break up the clusters of crystals and to insure maximum plasticity. Under these conditions, the product emerges from the crystallizing unit in a semi-liquid condition. In the case of margarine, which is commonly formed into solid prints in automatic machines, it is desirable to have it emerge as firm as possible. This is accomplished by allowing the material to crystallize with the minimum of agitation. The margarine 'B' unit therefore, is a straight tube 7 in. (18 cm) in diameter, made up of 18 in. (46 cm) sections to permit variations in length in accordance with the physical characteristics of the fat being solidified. The maximum 'rest' is given to the product by using two 'B' unit tubes, with the flow of product alternately directed by a motor-driven rotary valve. The cycle is so timed that the product which has been at rest is pushed out by the incoming product fresh from the chilling unit. At the point where the crystallized product has been replaced by the incoming product, the rotary valve diverts the flow to the other unit, and the newly filled unit comes to complete rest. This cycle is normally about 25 sec. During this rest period, crystallization of the supercooled emulsion takes place, and due to the heat of crystallization, the temperature rises 10–15°F (5·5–8°C). Normally there is no further temperature increase.

C. The complete process of margarine manufacture

In all modern processes there are essentially six steps, regardless of the type of equipment used. These are:

(a) Mixing of oil with oil soluble ingredients.
(b) Mixing of milk, cultured milk, salt and benzoate.
(c) Mixing of (a) and (b).
(d) Chilling the emulsion so formed.
(e) Forming prints of the chilled emulsion.
(f) Wrapping, cartoning and packing the prints.

In the first step, the required amount of oil is weighed and dropped into a stainless steel tank equipped with an efficient agitator. The temperature of the oil should be about 115–125°F (40–50°C). The amount of oil varies, depending on the size of the equipment and the practice of the individual manufacturer. A batch may be sufficient to run only a few minutes, or it may be large enough to run a machine an entire day.

With agitator running, the proper amounts of lecithin, monoglycerides and diglycerides, vitamin, A and artificial colour and flavour are added. It is customary to dilute the lecithin with liquid oil to reduce its viscosity and promote mixing. Because of the high melting point of the glycerides, they are also commonly diluted with several times their weight of margarine oil and added hot (140–145°F, 60–63°C). The small amounts of vitamin A, colour and flavour

also make it advisable to dilute them considerably with liquid oil, to facilitate uniform and rapid mixing.

When the oil-soluble ingredients are thoroughly mixed, the proper amount of milk, with the salt and sodium benzoate dissolved in it, is added. Since the finished margarine must contain at least 80 per cent fat, the amount of non-fat material must be not more than 20 per cent. In practice, most margarine manufacturers allow a slight overage of fat as a safety factor, so the amount of milk mix is slightly under 20 per cent.

After the milk is added, the mixture must be kept under rapid and constant agitation, for if mixing is stopped before the emulsion is chilled, the two phases immediately separate. Margarine is a stable emulsion only by virtue of the fact that the congealed oil contains the dispersed aqueous phase; in the liquid form the emulsion is maintained only by constant agitation.

The completed mixture is then rapidly chilled, either by the water chilling method, the chill-roll, or by passage through the Votator. The object of rapid chilling is two-fold. One purpose is to stabilize the emulsion, and the second is to produce a smooth, homogeneous product of fine crystal structure and free of graininess.

If the water crystallization or chilled roll method is used, the crystallized material is worked until it is homogeneous, the moisture and salt are adjusted to the desired levels, and the product is then placed in trucks in a refrigerated room (45°F, 7·0°C) for several hours, to become firm enough to print.

If the continuous system is used, the emulsion is pumped through the chilling 'A' unit, to the crystallizing 'B' unit, and extruded in a form suitable for forming prints.

The continuous closed system offers the advantages of sanitation, labour economy and refrigeration efficiency. It is also easier to produce a uniform product, since the control over temperature and flow rate is much more precise.

The chief objection to the Votator system is that the violent agitation in the chilling unit produces an extremely fine dispersion of the milk droplets in the fat. While this tight emulsion is effective in preventing leakage of moisture from the margarine, it produces a product with a 'slick' or 'greasy' appearance. In addition, the tight emulsion delays the release of the milk flavour in the mouth, for the surrounding fat must melt before the fine droplets of milk can coalesce sufficiently to become perceptible to the organs of taste. Also, the fine crystal structure and the crystallization with the minimum of agitation produce a less plastic product.

The adherents of the chill-roll system, which is still largely used in Europe, claim that their method produces a margarine with a more butter-like consistency and appearance. There is considerable justification for these claims, but in the interest of efficiency, practically all United States and Canadian margarine is made by the Votator process, and the people in these countries have apparently become accustomed to the physical properties of this type of margarine.

In an effort to overcome some of the drawbacks of the tight-emulsion Votator process, a number of methods have been tried. Three patented methods are in

limited use today. One of these methods involves opening the structure of the emulsion by dispersing part of the aqueous phase in larger droplets; another selectively crystallizes a high percentage of glycerides melting at or slightly below body temperature; and the third involves growing of large aggregates by churning.

D. The milk injection process

This process, patented by MILLER (1943) consists of proportioning most of the milk into the chilled emulsion after if emerges from the 'A' unit. A five cylinder pump of sanitary design proportions the milk into the chilled emulsion, as well as serving as the product pump.

It is necessary to incorporate 10–15 per cent of the milk into the fat to avoid the appearance of translucent spots of pure fat in the finished product. This portion of the milk may be cultured and unsalted, if desired, so that further bacterial action in the finished product can take place. In any event, the fat and fat-soluble additives, with a portion of the milk are pumped by four cylinders of the five-cylinder pump through the 'A' unit of the Votator. The other cylinder meanwhile pumps the milk–salt mixture through a tubular milk cooler, and the two streams join at a blender. The blender consists of a cylinder in which a shaft fitted with pins in a spiral position revolves. These pins mesh with stationary pins in a comb form attached to the top of the cylinder wall. The blending action of these meshing pins incorporates the milk with the supercooled fat portion, but the dispersion is not nearly so fine as that occurring when the entire emulsion is subjected to the violent agitation in the chilling unit. The speed of the blender must be adjusted to the throughput rate of the product, so that sufficient dispersion is accomplished to keep the aqueous phase from separating from the mass, but it must not be so violent as to produce too fine a dispersion. The blended mixture is discharged as usual into the quiescent 'B' unit for crystallization.

The product made by the milk injection process is said to be characterized by the speed with which the milk flavour becomes apparent when the margarine is placed in the mouth. Additionally, it is claimed that this margarine has a saltier taste than a margarine with the same percentage of salt but made by the conventional Votator process, and that it also has a less greasy appearance.

E. Pre-crystallization process

WILSON *et al.* (1952), have patented a method for improving the quickness of melt and the spreadability of margarine by inducing the growth of a higher precentage of large size crystals melting at body temperature or slightly below. Essentially the method involves introducing part of the chilled and emulsified mixture discharged from the 'A' unit into the warm emulsion entering the 'A' unit. Both streams are brought together in an apparatus similar to but larger than the blender (above), the discharge of which is connected with the chilling unit. As the stream of chilled fat emulsion is mixed with the warm emulsion of identical composition, it is claimed that the crystals of the lower-melting glycerides melt, leaving a high percentage of crystals that melt at or near body

temperature. It is probable that these solids also act as seed crystals and promote growth of larger crystals. Internally, it is believed that the larger crystals are imbedded in a matrix of minute crystals of lower melting point which hold the liquid components. Because of this, it is claimed that the melting in the mouth is much more rapid than with conventional margarine, and the spreadability at low temperature is improved.

Ratios of chilled to unchilled emulsion range between 1 : 2 and 1 :1. The chilled emulsion emerges from the 'A' unit at 50–60°F (10–15°C), the warm fat enters the pre-crystallizing unit at about 100°F (38°C) and the mixture enters the 'A' unit at about 85°F (29°C). The portion of the chilled emulsion not returned to the precrystallizer is passed through a series of screens (Rourke and Dow, 1948) and baffles designed to cause sudden changes in direction of flow. This produces a thorough mixing and working to produce a smooth product. From the screens the worked product goes to the usual quiescent 'B' unit.

F. Steam injection and churn process

Turgasen (1950) has patented a method of margarine manufacture that closely follows the churning procedure for making butter. The process was developed on the premise that each globule of milk fat is coated with a loose protective phospholipid–protein film. Lack of film continuity exposes fat surfaces, and during churning globules adhere together at the point of film interruption to form granules.

To accomplish this in margarine Turgasen brings together the melted fat and milk in proportions of about 1 part fat to 2 of milk. The mixture is pumped in a vessel and steam injected in the direction of flow. The injected steam raises the temperature to about 250°F and disperses the continuous oil phase into a fat-in milk emulsion. The heated mixture is flashed into a vessel held under about 25 in. (63·5 cm) vacuum, where the dispersion of fat in milk is completed and a heavy cream-like emulsion is obtained. The emulsion is cooled over a milk cooler until the temperature is well below the melting point of the fat. At this point milk cultures may be added, and the emulsion incubated for flavour.

The emulsion is then churned in the conventional manner used in making butter. After the emulsion reverses, draining, washing, salting and moisture adjustments are carried out in the same manner as in butter making. After churning, the product is removed to trucks and tempered at low temperature for several hours before packaging.

Each of these methods has certain advantages and certain limitations, as does the conventional Votator process. The choice of method is based on the opinion of the individual margarine manufacturer as to the type of process which makes the kind of margarine best suited to his trade. High quality margarines are being made in the United States by several of these methods.

VI. Margarine Packaging

Margarine for household consumption, as well as butter, has for many years been marketed in individually wrapped 1 lb or ¼ lb prints. Probably, in the beginning,

the margarine was formed into single prints by hand using moulds similar to those still used on the farm for printing butter. Later, these moulds were replaced by boxes holding about 90 lb equipped with loosely fitting bottoms. The margarine was tamped into these boxes and then covered with a frame having cross wires spaced in both directions. A ram then raised the loose bottom, forcing the margarine up through the crossed wires. When the desired height was

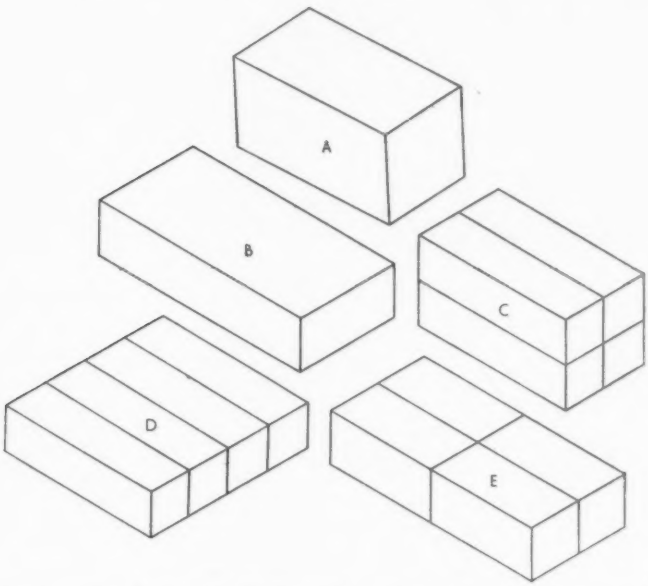


Fig. 4. (a) Elgin 1 lb print; (b) Western Flat 1 lb print; (c) Elgin 1 lb print; (d) Eastern Flat ¼ lb prints; (e) Western Flat ¼ lb prints.

reached, a wire bow was drawn across the top, cutting the portion above the box into several prints. These prints were then wrapped by hand.

Later an extruder was developed which, by means of spiral screws, forced the margarine through a rectangular forming nozzle having two of the dimensions of the desired print. The emerging slab was then cut at intervals by wires, fixed in a frame and drawn through the slab crosswise.

At present, automatic combination printing, wrapping and cartoning machines are offered by both American and European manufacturers. These machines usually have an open hopper, into which the margarine can be delivered directly from the Votator 'B' unit, or from trucks if the product is tempered before printing. Spiral screws feed the product into a printing mould. When the mould has been filled the print is discharged directly into an automatic wrapping machine, and then to a cartoner. These machines are efficient, have good weight control, and are desirable because of the minimum handling of the product required.

Previous to the repeal of the tax on coloured margarine in the United States, most margarine was sold uncoloured in solid 1 lb prints, and a packet of powdered dye sufficient to colour 1 lb was supplied with each print. Since 1950, because of the convenience to the housewife, practically all coloured margarine is packaged in $\frac{1}{4}$ lb prints. The shape of these prints has followed the style established by butter, and it is interesting to trace the evolution of packaging styles. The original package popular in the eastern United States was the 'Elgin' 1 lb print (Fig. 4a). This was a print that was square in end section, the dimensions being $2\frac{1}{2}$ in. $\times$ $2\frac{1}{2}$ in. $\times$ $4\frac{3}{4}$ in. (6·35 cm $\times$ 6·35 cm $\times$ 12·07 cm). At the same time, in western United States, the popular package was the 'western Flat' print (Fig. 4b.). This print was thinner, wider and longer than the Elgin, being $1\frac{1}{2}$ in. $\times$ 3 in. $\times$ $6\frac{1}{2}$ in. (3·81 cm $\times$ 7·62 cm $\times$ 16·51 cm). About 1945, the Western Flat 1 lb print was adopted by most eastern manufacturers, and this was the standard margarine print until repeal of the colour law and the subsequent popularity of the $\frac{1}{4}$ lb print. The eastern manufacturers then returned to the Elgin $\frac{1}{4}$ lb print (Fig. 4c). This was essentially the Elgin 1 lb quartered by cutting from top to bottom and one side to the other on the minor axis, giving dimensions of $1\frac{1}{4}$ in $\times$ $1\frac{1}{4}$ in. $\times$ $4\frac{3}{4}$ in. (3·18 cm $\times$ 3·18 cm $\times$ 8·25 cm). The four prints were then cartoned to resemble the original print; i.e. two on two Later, the four prints were placed side by side to make a flat, almost square package, 5 in. $\times$ $4\frac{3}{4}$ in. $\times$ $1\frac{1}{4}$ in. (12·70 cm $\times$ 12·07 cm $\times$ 3·18 cm). This is referred to as the 'Eastern Flat' package and currently is the favourite in the east (Fig. 4d). At the same time, the westerners preferred their Western 1 lb print quartered by equally dividing from top to bottom both the major and minor axes, producing a print $1\frac{1}{2}$ in. $\times$ $1\frac{1}{2}$ in. $\times$ $3\frac{1}{4}$ in. (3·81 cm $\times$ 3·81 cm $\times$ 8·25 cm). These quarters are currently cartoned in the form of the original Western 1 lb print (Fig. 4e).

Practically all United States margarine is packaged in one of the above forms. One brand of Canadian margarine, and some European brands are packaged in two $\frac{1}{2}$ lb prints. These prints are in a shape similar to the Eastern Flat, being $2\frac{1}{2}$ in. $\times$ $1\frac{1}{4}$ in. $\times$ $4\frac{3}{4}$ in. (6·35 cm $\times$ 3·18 cm $\times$ 12·07 cm).

Some margarine for export is packaged in 1 lb sealed tins, and bulk bakers' margarines are commonly packed in 50 lb cans or 400 lb steel drums. These margarines are processed similarly to shortening. After the chilled emulsion leaves the 'A' unit, it goes to a 'B' unit providing agitation during the crystallizing period. This product emerges from the 'B' unit as a semi-liquid, and it requires several minutes for it to set up. Packed while in this semi-liquid state, it spreads out and completely fills the container.

The preferred wrapper for butter or margarine was, and to some extent still is, vegetable parchment. From the cost standpoint, parchment is a very efficient wrapper. It supplies a clean, greaseproof wrap of attractive appearance. Parchment, however, in spite of its grease resistance, offers little or no protection against loss of moisture on storage, or exclusion of oxygen.

A few years ago, the aluminum foil wrap was introduced as an added protection, since it does furnish an effective vapour-transfer barrier. Colourfully

printed and neat in appearance, the foil wrap became immediately popular with the consumer, and now nearly all the quality margarines in the United States are foil wrapped. The foil usually used is 0·00035 in. aluminum foil, laminated to a parchment or sulphite paper liner. The laminating material may be wax, but on becoming soaked with grease, the wax dissolves and delamination occurs. The preferred laminating material is a thermoplastic vinyl resin. The paper backing may or may not be treated with melamine resin to improve wet strength. The foil side of the wrap is usually treated with a coating material to protect the aluminum from corrosion, and to give the material the necessary 'slip' to run properly in the automatic wrapping machine.

A revolutionary packaging material was introduced in 1947 by PETERS (1944). This was a plastic bag containing a gelatin capsule of liquid colour attached to the wall of the bag. The bag was filled with margarine and heat-sealed. To colour the margarine, the gelatin capsule was ruptured, and the colour was evenly worked in by gently kneading the sealed bag. This greatly facilitated the colouring of the margarine, and it was an instant success. The repeal of the tax on coloured margarine has eliminated the sale of this product except in the states of Wisconsin and Minnesota, which prohibit the sale of coloured margarine. The Peters bag is still popular in Canada, where at present only one province allows the sale of coloured margarine. The margarine for the Peters bag was somewhat softer than printed margarine, and it was manufactured like bulk margarine (above). The plastic bag was most commonly made from pliofilm, although certain vinyl films were successfully used. The primary requisites of a film for this bag were the ability to make a tight, strong heat seal, and the toughness to withstand kneading and possible puncture by fingernails.

Margarine in the United States is almost universally encased in a waxed carton. The carton protects the inner wrap from damage, and what is very important, affords rigidity and protection to the product in stacking and handling. The cartons are usually of 16 point virgin board of good quality, and they are heavily waxed. In order to feed and fold properly on automatic equipment, the cartons must have the proper rigidity, must be scored properly, and have a good 'slip'.

When parchment inner wraps were commonly used, some manufacturers used a heat-sealed waxed paper or cellophane overwrap over the waxed carton for the sake of additional protection. With the popularity of the aluminum foil wrap, overwraps lost much of their value, and are now only occasionally used.

A recent innovation in overwraps is a laminated, heat sealable, foil overwrap. In combination with the foil inner wrap, this is claimed to give greatly improved protection to the product.

VII. Margarine Spoilage Problems

A. Rancidity

Margarine is not subject to the sort of 'rancidity' that butter suffers from, which is a result of the hydrolysis of the glycerides of the short-chain fatty acids

with the release of the strong-smelling volatile acids such as butyric, propionic and valeric.

The type of rancidity to which margarine is subject is the oxidative rancidity common to the usual fats and oils. This results in the characteristic flavour change which is caused by oxidation of unsaturated fatty acids.

Practically speaking, with modern hydrogenation practices, with reasonable care in handling the oil, and with reasonable refrigeration in storage, rancidity is hardly a problem with modern margarine.

B. Bacterial spoilage

Due to its content of milk and moisture, margarine will support the growth of certain types of mould, and mould is probably the largest single cause of margarine spoilage.

Sodium benzoate is an efficient inhibitor of mould growth, provided the pH is sufficiently low. The trend toward lesser amounts of cultured milk has largely, but not entirely, nullified the effectiveness of sodium benzoate.

Salt, also, to a large extent inhibits the growth of mould, and the heavier salted margarines are less susceptible to mould growth than the lightly salted or unsalted ones.

Packaging materials, such as aluminum foil and the plastic bag, which exclude air from the surface of the margarine effectively suppress the growth of mould.

However, the best defence against mould is prevention of contamination, and this involves good plant housekeeping.

A margarine plant must be scrupulously clean, and there is no substitute for the scrub brush, detergent and plenty of hot water. All process lines and equipment which have been in contact with milk or emulsion or margarine should be washed free of their film of milk or oil by means of a scrubbing brush and an efficient detergent at the close of the day's operations. The equipment should be thoroughly rinsed with plenty of hot water. At the beginning of the day's operations, equipment should be washed with an efficient sterilizing solution, followed by a rinse of plain water.

Preferred sterilizing solutions are either hypochlorite or one of the commercially available quaternary ammonium compounds.

In locations where powdered milk dust is liable to collect on walls, ceilings or fixtures, or where liquid milk is liable to spatter, walls and ceilings should be washed with sterilizing solution, rather than rinsed, for lasting effect. This should be done at intervals ranging from daily to weekly, depending on the extent of contamination. Walls and ceilings of the processing rooms should be washed periodically in the same way. For washing walls, some margarine manufacturers recommend that hypochlorite and quaternary ammonium solutions be alternated, so that the organisms cannot build up an immunity to one sterilizer. At the same intervals, the atmosphere may also be sterilized by fogging the rooms by means of an efficient atomizer.

Product pipelines are of the sanitary type to permit taking down for cleaning. Recent installations of cleaned-in-place pipelines in some dairies have aroused

interest among margarine manufacturers, and these may well be adopted soon. Essentially, cleaning-in-place means just that. Instead of taking down pipelines for cleaning, provision is made for the rapid circulation of solutions through the lines, which effectively cleans and sterilizes them. Careful consideration must be given to the rate of flow of the solutions, the proper drainage of the lines, and particularly the temperature of the solutions; but when properly done, it is claimed that the cleaning is rapid and effective. Cleaning-in-place has the obvious advantages of labour saving, less wear and tear on fittings, and less chance of re-contamination while replacing pipelines.

Tanks and equipment handling oil only need not be of stainless steel, and most are of conventional mild steel. Although strenuous sanitary precautions are unnecessary, it is as well to avoid the accumulation of films of oxidized oil on the sides of storage tanks. Therefore, storage tanks should be periodically brushed thoroughly with plenty of hot water (no detergent). The cleaning should take place just prior to complete refilling of the tank, to avoid rust.

Pipelines handling oil should either be left completely full of oil, if this can be done without the oil setting up, or provided with a means of blowing the lines with nitrogen or other inert gas. Preferably, means should be provided to close the lines while they are full of inert gas if they are not going to be used for some time.

As a means of preventing airborne contamination, some margarine plants are 'pressurized'; i.e. a pressure slightly higher than that of the outside air is maintained in process rooms by means of blowers pumping filtered air.

The preferred system, which is being done in most new plants, is complete air-conditioning, where all the air is filtered, washed and temperature-controlled the year round, thus ensuring the absence in the air of mould spores, dirt or insects.

It is obvious that the margarine plant must be kept completely free of all rats, roaches, flies and other insects. This can be done by air-conditioning, or efficient screening plus a regular programme of spraying. Rats are best controlled by keeping trash and other debris from collecting, plus constant vigilance and a regular inspection by a qualified professional exterminator.

VIII. Special-purpose Margarines

To satisfy the requirements of commercial bakers for margarines designed for specific jobs, some special-purpose margarines have been developed. These special purpose margarines are sold in bulk, in 5 lb loaves, 50 lb tins or 400 lb drums.

A. Margarines for baking

The special margarines for baking are designed primarily to give flavour to baked goods and icings, and thus they are usually much more highly flavoured than table margarines. Margarine does not contain the high percentage of monoglycerides and diglycerides that the super-glycerinated or 'high-ratio' shortenings do, so does not have the emulsifying power of the shortening. Therefore, in cakes and icings, bakers' margarines are used in combination with the super-glycerinated shortening. The amount of margarine varies from 15 to 50

per cent of the total fat, depending on the individual baker. Since bakers' margarine is used in combination with shortening, the consistency is usually made the same as shortening. Bakers' margarine is also frequently used alone in cookies and in Danish pastries.

B. Danish roll-in

Danish pastry derives its richness and characteristic flakiness from the 'rolling-in' of a liberal amount of fat after the dough is mixed.

A Danish pastry dough is very extensible and reasonably tough, but if the fat is too hard or brittle, it has a tendency to puncture the dough during the rolling-in operation. On the other hand, if the fat is too low in melting point, it will melt down during the proofing operating (incubation at a warm temperature to accelerate the growth of the yeast and thus the rising), and the dough will become grease-soaked and soggy. Therefore, what is desired for a Danish roll-in margarine is a product with the maximum plastic range. Danish roll-in margarine may be made from either a combination of hydrogenated and liquid vegetable oils, or a combination of liquid vegetable oils and animal fat. Either the all vegetable oil or the vegetable oil–animal fat product can be made with an excellent plastic range.

C. Puff-paste

The third class of special-purpose margarines is the so-called 'puff-paste', designed for making pastry shells and French pastries. The dough for this pastry is a tough, unleavened, unsweetened dough. The pastry gets all its 'spring' in the oven from the expansion of the moisture entrapped in the fat between the layers of dough.

A tough, waxy fat of maximum extensibility is required for puff-paste. The usual puff-paste fat sold in the United States is a combination of 35 per cent oleostearine and 65 per cent liquid cottonseed oil.

Puff-paste was usually emulsified with 6–8 per cent of water. Since the repeal of the margarine tax laws, most puff-pastes are made with milk, but the percentage of moisture is kept the same.

D. Salt-free margarine

A limited amount of salt-free margarine is made in the United States. This is mostly used commercially in the making of imitation whipped cream toppings and the like. The chief difficulty with this product is the poor keeping quality, for the lack of salt makes it extremely susceptible to mould growth.

E. Dietetic margarine

For those consumers whose religious beliefs forbid eating any animal product, or who, for dietetic reasons, must eliminate cow's milk from the diet, there is limited distribution of the product made from soybean oil in which a suspension of finely ground soybeans in water is substituted for the skim milk. This is a fair simulation of margarine; but it probably will never be in large demand.

Although the principal use of conventional margarine is as a table spread, it also serves to a large extent as the all-purpose fat for the average user. Margarine is used extensively as a shortening in household baking, for seasoning vegetables, and for sautéing. Particularly in the northern European countries and in United States communities where people of Northern European extraction predominate this is true, for traditionally they are accustomed to using solid fats in cooking.

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